Modeling the impact of fuel properties on spark ignition engine performance

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ABSTRACT OF THE
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Even today transport sector is heavily dependent on fossil fuels, contributing at the same time to significant part of global greenhouse gases emission. Advanced transport drop-in fuels based on renewable feedstock are the most effective way of decreasing the environmental impact of the entire sector. This work is a part of ADVANCEFUEL EU project which is aiming at the promotion of renewable transport fuels by providing new knowledge, tools, standards, and recommendations to minimize the most significant barriers towards commercialization. The main goal of this thesis is modeling the impact of fuel properties on spark ignition (SI) engine performance and carbon dioxide emissions. The results include models (based on multi-linear regression) that represent the impact of octane number, heat of vaporization, net calorific value and auto-ignition temperature on fuel consumption and carbon dioxide emissions from the end-use point of view. Modeling work was performed based on results from the driving cycles such as New European Driving Cycle (NEDC) and Worldwide harmonized Light vehicles Test Cycle (WLTC), where both input and output parameters are represented by percentage changes relative to standard gasoline fuel. Using alcohol-gasoline blends yielded higher fuel consumption in all cases. The model's prediction accuracy is very high and the values are close to measured ones (average absolute error 1,2%). Based on chosen sources, the highest fuel consumption was observed for E85 fuel blend. In that case model predicts 46,89% change of fuel consumption compared to standard gasoline. The prediction of carbon dioxide emissions is based on outcomes of fuel consumption model. Supplementarily, fuel blend property calculator was created in order to predict alcohol-gasoline fuel blend properties.

Keywords: model development, system identification, alternative fuels, fuel blend properties, SI engine performance, fuel consumption, CO2 emissions

Preface

This thesis is the final part of my Innovative Sustainable Energy Engineering studies at Joint Nordic Master's programme. I started my first year at KTH Royal Institute of Technology in Stockholm (Sweden), while the second one continued at Aalto University in Espoo, Finland. This work is a part of EU Horizon 2020 projects (ADVANCEFUEL) conducted in the Thermodynamics and Combustion Technology Research Group at Aalto University. I started working on the thesis since June 2016, where additionally I was assisting Bioenergy I, Power Plants and Processes and Combustion Technology courses. During that period I broadened significantly my knowledge regarding both internal combustion engines and alternative fuels designed for the transport sector. I was delighted having the possibility of working on this project, from many perspectives. I am interested in renewable transport fuels and internal combustion engines, hence it was a great chance for me to develop myself in the area that I would like to become an expert. I want to thank warmly my supervisor Professor Martti Larmi for offering me this opportunity and helping me throughout all period with professional advice. I want to thank my advisor Ossi Kaario for highly valuable comments and tips. Additionally, I would like to thank Kai Zenger for a great assistance during system identification and mathematical modeling stage. Moreover, I am highly grateful, to Mika Aho and Börje Kronström from ST1, Daniel Danielsson and Sten Hovmark from AVL, Anders Röj and Per Hanarp from VOLVO and Teemu Sarjovaara from NESTE for cooperation and very valuable advice. I would like to also thank Thomas Kohl for cooperation during the ADVANCEFUEL project.
I am particularly thankful to my family, wife (Marianna), mother (Anna), father (Gagik), sister (Arpenik), grandmothers (Hranush and Juleta) and grandfathers (Yuri and Gurgen) for motivation and support. Finally, I would like to strongly thank my friend Michal Wojcieszyk with whom I was working on the project.

Otaniemi, April 26, 2018

Yuri Kroyan

Contents

Symbols and abbreviations

Symbols

Operators

Abbreviations

AFR	Air-to-fuel ratio
ASTM	American Society of Testing and Materials
BDC	Bottom dead center
SI	Spark ignition
CI	Compression ignition
CNG	Compressed natural gas
DF	Dual fuel
DI	Direct Injection
GPF	Gasoline particulate filter
EGR	Exhaust gas recirculation
EN	Eurpoean norm
HC	Hydrocarbons
ICE	Internal combustion engine
IDI	Indirect Injection
ISO	International Organization for Standardization
DI	Direct Injection
PFI	Port Fuel Injection
MPFI	Multi-Port Fuel Injection
LPG	Liquified petroleum gas
LTC	Low temperature combustion
PM	Particulate matter
RCCI	Reactivity controlled compression ignition
SCR	Selective catalytic reduction
SI	Spark ignition
TDC	Top dead center
TWC	Three-way catalyst
RESfuels	Renewable Energy Source fuels
MTBE	Methyl Tert-Butyl Ether
ETBE	Ethyl Tert-Butyl Ether
TAME	Tert-Amyl Methyl Ether
TAEE	Tert-Amyl Ethyl Ether
DIPE	Di-Iso-Propyl-Ether
VLI	Vapor Lock Index
RON	Research Octane Number
MON	Motor Octane Number
NCV	Net Calorific Value
NCVmass	Net Calorific Value mass based
NCVvol	Net Calorific Value volume based
GCV	Gross Calorific Value
NVP	Net Vapor Pressure
HoV	Heat of Vaporization
AIT	Auto Ingnition Temperature.

FBPC	Fuel Blend Property Calculator
VP	Vapor pressure
BMEP	Brake Mean Effective Pressure
MPS	Mean Piston Speed
TPS	Throttle Position Sensor
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal Efficiency
MBT	Maximum Brake Torque
LHV	Lower Heating Value
WOT	Wide Open Throttle
EDC	European Driving Cycle
UDC	Urban Driving Cycle
EUDC	Extra-Urban Driving Cycle
NEDC	New European Drive Cycle
LPV	Low-Powered Vehicles
WLTP	Worldwide Harmonized Light Vehicles Test Procedure
E5	Fuel: blend of ethanol 5% and Gasoline 95%
E10	Fuel: blend of ethanol 10% and Gasoline 90%
E20	Fuel: blend of ethanol 20% and Gasoline 80%
E30	Fuel: blend of ethanol 30% and Gasoline 70%
E40	Fuel: blend of ethanol 40% and Gasoline 60%
E50	Fuel: blend of ethanol 50% and Gasoline 50%
E60	Fuel: blend of ethanol 60% and Gasoline 40%
E70	Fuel: blend of ethanol 70% and Gasoline 30%
E80	Fuel: blend of ethanol 80% and Gasoline 20%
E90	Fuel: blend of ethanol 90% and Gasoline 10%
E100	Pure ethanol fuel
iBu	iso-Butanol
nBu	n-Butanol
rpm	rotations per minute
MISO	Multiple Input, Single Output
LMA	Levenberg-Marquardt Algorithm
OEM	Original Equipment Manufacturer
FC	Fuel Consumption

Chemical compounds

CO_2	Carbon dioxide
H_2O	Water
NO_x	Nitrogen oxide
PM	Particulate Matter
HC	Hydrocarbons
CH_3OH	Methanol
C_2H_5OH	Ethanol
MMT	Methylcyclopentadienyl Manganese Tricarbonyl

1 Introduction

World greenhouse gases (GHG) emission have increased significantly over the past two decades, which resulted in perceptible local climate changes at different places in the world. Carbon dioxide is responsible for a majority of global GHG emissions. In that sense, by decreasing emissions of carbon dioxide to some safe level, climate change can be prevented. Carbon dioxide emissions are coming from different sources, such as electricity and heat production around 42%, transport 29%, industry 12%, residual emissions, services and others [6]. The transportation sector is a second larger contributor to GHG emissions, and its share of the sectors have increased from 1990 to 2015 in about 5% [7]. In general, branch could be divided into air, road, rail and water modes, this work is focused on automotive road transportation. Where special attention is devoted to how fuels and fuel blends properties affect engine performance, with respect to efficiency, emissions and necessary technology update in end-use.

The motivation of this work is a support of market roll-out facilitating process of renewable energy source fuels (RESfuels) in the transportation sector. RESfuels in comparison with fossil fuels are sustainable, due to the fact that their feedstock is renewable. Biomass, which is utilized to produce biofuels, absorbs carbon dioxide from the air and with the water and minerals that are extracted from the ground, builds up its tissue and grows. Thus, during combustion, the same amount of carbon dioxide is released into the air, that has been taken from the air. Consequently, the average amount of carbon dioxide remains unchanged. Another important aspect is that fossil fuels are limited, which means that their price will rise with a time. Biofuels can offer relatively stable price over time and cover a significant part of the demand when fossil fuels will run out.

The objective of this work is a development of a numerical tool in an open source format, that will predict fuel and fuel blend properties impact on efficiency of spark ignition engine and emissions in end-use. This work consists of background, methodology and results parts. In the first part engine characteristics are studied with special attention on classification of engines, operational principles, engine operating parameters, engine efficiency and components. Additionally, combustion processes and related issues such as knocking combustion and relatively new phenomena called super-knock are discussed. Further parts of the background section are focused on fuel characteristics, where important fuel properties and mandatory standards, exhaust emissions and their control technologies are analyzed. The second part of the thesis is sacrificed for chosen methodologies regarding fuels and fuel blends selection, the distinction of the most influential properties of fuels that affect engine performance and emissions. Additionally, for the purposes of this work Fuel Blend Property Calculator (FBPC) was developed. Subsequent chapters are focused on detailed approach where in order to achieve high universality of the models driving cycles were selected as a base of input and output data. The final part of the methodology section includes mathematical modeling approach selection and chosen validation

techniques. Results section represents the final model for fuel combustion analysis and carbon dioxide emissions its validation outcomes and carbon dioxide emissions prediction formula. Last part of this work concludes entire work with attention on limitations, the importance of the research and further recommendations.

1.1 ADVANCE*FUEL* project

The advance fuel project is a part of EU Horizon 2020 projects in response to the LCE 21 call (Low-Carbon-Energy), which is aiming at providing clear and scientifically robust support for sustainable transport fuels. The main target of the project is to facilitate the market roll-out of advanced liquid biofuels and other liquid renewable fuels in the transportation sector between 2020 and 2030, with an outlook on post-2030 impacts. The goal will be achieved by providing the market stakeholders with state of art knowledge, and sophisticated, user-friendly tools with integrated calculators, standards, and recommendations. Given knowledge and tools, will support decision makers to remove the most prominent barriers against the commercialization of renewable energy source fuels ("RESfuels"). In order to accomplish the task the project is spat into eight specific objectives and ten work packages:

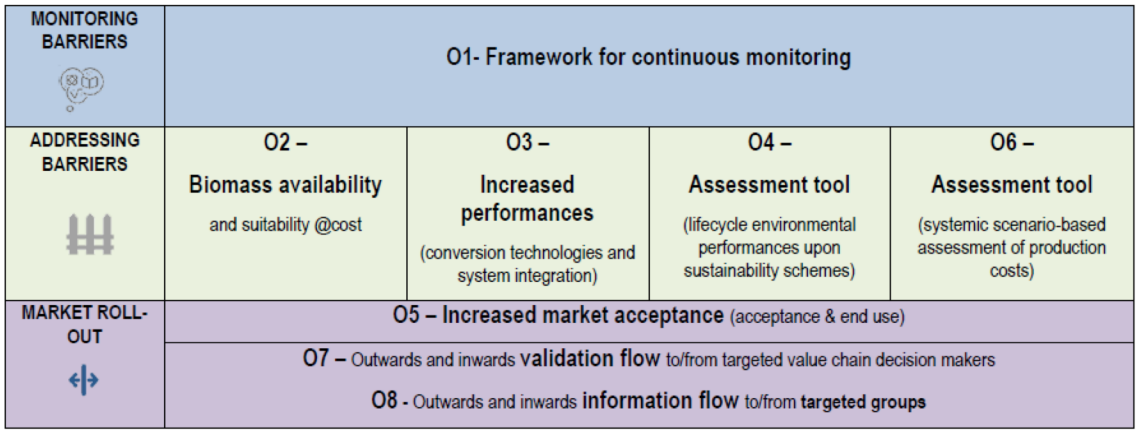


Figure 1: ADVANCE*FUEL* projects' objectives [1].

This work is a part of objective O5: "recommend measures to increase market acceptance and end use of RESfuels based on a detailed market segmentation ac-

counting for the role of fuel and fuel blend properties". Specific work packages are presented in the Figure 2, where WP5 "Improve evidence for market uptake" is the target of this thesis.

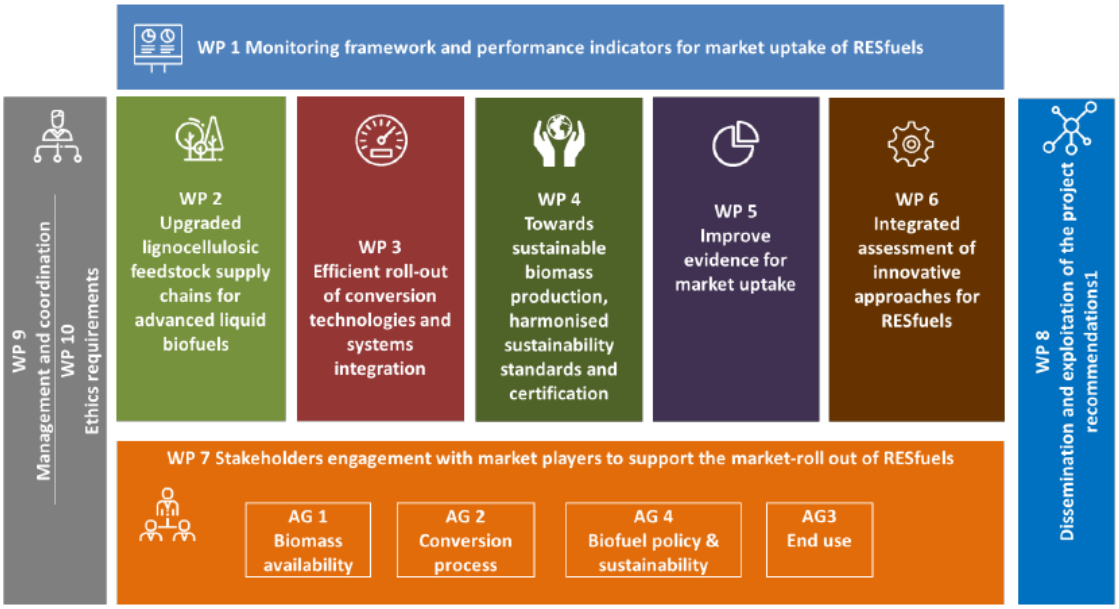


Figure 2: Approach to the **ADVANCE***Fuel* project - work packages [1].

The purpose will be achieved by development of a numerical tool in an open source format as a spreadsheet programme. The tool is developed on models and methods based on the most relevant and recent knowledge obtained from publications in journals, conferences, work shops with end-use stakeholders and international energy agency (IEA).

Objective	Output	Expected Impact	Measured Impact
Tailored tools addressing fuels blending properties in end use	Numerical tool	Improved understanding on fuel blending properties	Stakeholders able to use a common set of numerical tools addressing fuels blending properties in end use

Table 1: Expected impacts brought by the support activities outputs beyond the LCE 21 call.

The research work was carried out in the Group of Thermodynamics and Combustion Technology led by Professor Martti Larmi. The main activities of Aalto Group include Experimental Engine Combustion Research (low-temperature combustion in dual fuel engines, alternative fuels and spray diagnostics, optical measurements on high-pressure fuel injection and mixing) and Advanced Computational Energy Research (ignition and combustion in gas and dual fuel combustion, CFD of chemically reacting flows and heat transfer, computational fluid dynamics fundamentals). There

are 8 partners working on the project: FNR (coordinator), ECN, Utrecht University, Imperial College London, Chalmers University of Technology, Greenovare! Europe, ATB and Aalto University (Figure 3).

Figure 3: Partners of ADVANCE*FUEL* project [1].

Main stakeholders of Aalto University group are ST1[3], NESTE OIL[2], VOLVO[4] and AVL[5].

Figure 4: Main Stakeholders of ADVANCE*FUEL* project from Aalto University group [3], [2], [4], [5].

1.2 Scope of the project

The scope of this work covers examination of fuel blend properties impact on SI engine performance indicators and carbon dioxide emissions. Where project's second part made by Michal Wojcieszyk include measuring the impact of fuel properties on CI engine performance. Those two parts together characterize light-duty vehicles section. However, the project includes also off-road, marine and aircraft engines, that will be developed in the future. The work is divided into five parts, literature study, data collection, data analysis, development of numerical tool and master thesis. During first part necessary theoretical background was studied, where subsequent three parts were devoted to the core part of this work. The last stage was dedicated for master thesis finalization.

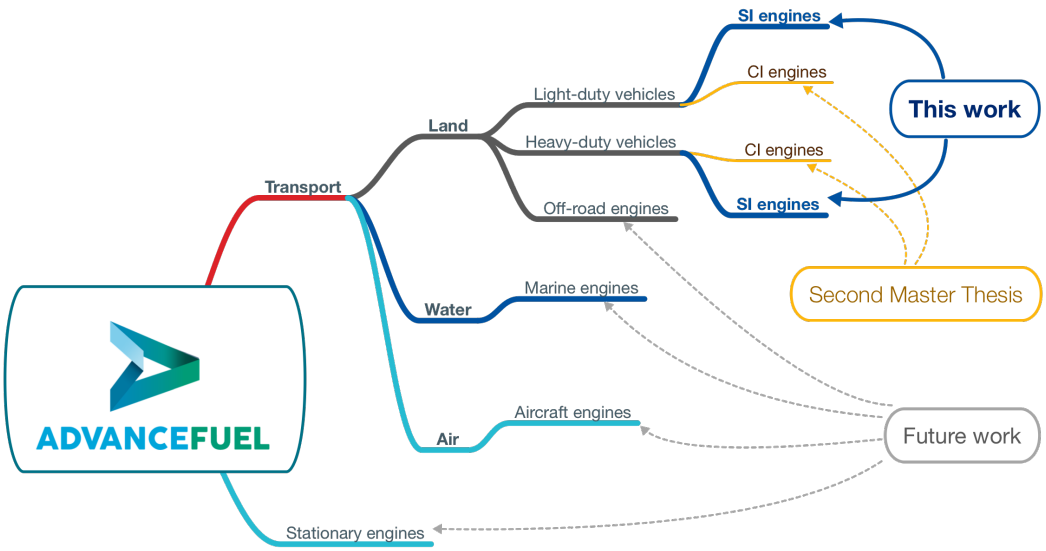


Figure 5: Scope of this work.

1.3 Task 5.4 - Fuel and fuel blend properties in end use

This work is related to the task 5.4 called *"Fuel and fuel blend properties in end-use"* from ADVANCE*FUEL* project. The purpose of task 5.4 is a creation of a numerical tool that predicts fuel and fuel blend properties in end use. Which in turn will support facilitating the use of Renewable Energy Source fuels (RESfuels) in the transportation sector.

1.4 Objectives

In order to meet the target stated in the task 5.4, work has been divided into several sub-objectives:

- Creation of numerical tool for fuel blend final properties prediction.
- Creation of numerical tool for prediction of fuel properties impact on fuel consumption.
- Creation of numerical tool for prediction of fuel properties impact on CO_2 emissions.
- Numerical tools shall be in an open source format as a spreadsheet programme.
- The tools and applied methods should rely on most relevant and recent knowledge
- Combining all tools into one with user-friendly infrastructure.

2 Background

2.1 Engine characteristics

Engine in general converts different forms of energy into mechanical power. There are three categories of engines, heat engine, electric motor and physically powered motor. The heat engine is a machine that converts heat into the work and includes two categories: combustion engine and non-combustion engine. Combustion engine produces heat through the combustion of a fuel, in an external or internal process. Internal combustion engines (ICE), burn the fuel inside the engine, producing heat which is subsequently converted into the work (drive). The ICE is widely applied in automobiles, motorcycles, ships, locomotives, and aircrafts. External combustion engine, such as steam turbine, produces work by an expansion of the steam inside the turbine. However, steam is produced outside the engine in a boiler, where the fuel is combusted. Non-combustion engines produce work without combustion process. That kind of engines is used in nuclear power plants, where steam is produced through the nuclear reactions and after that passes through the engine and produces power. The electric motor converts electrical energy into mechanical work, using the law of electromagnetism. Which concerns current passing through the coil within a magnetic field and producing a force that rotates the coil. These engines are widely applied in different categories of tools, vehicles, and etc.. due to the fact that they are relatively quiet, clean and work with high efficiency. Another group is represented by the physically powered motor, that is driven by kinetic or potential energy. This group is represented by pneumatic or hydraulic motors. The pneumatic motor converts potential energy stored in compressed air into mechanical work, whereas hydraulic motor produces power from a pressurized fluid.If it comes to internal combustion engines, there are two major types of engines, that are dominating the entire market. There can be distinguished so-called Otto engine (spark ignition) and Diesel engine (compression ignition). This work focuses on spark ignition (SI) internal combustion engines, with a history that reaches early 1800's. Franco-Swiss inventor, François Isaac de Rivaz (1752-1828) designed and developed world's first internal combustion engine in 1804, which was powered by a mixture of hydrogen and oxygen ignited by spark manually. Subsequently, in 1808 that engine was placed in the vehicle – "the world's first internal combustion powered automobile" [10]. However first commercially successful internal combustion engine was developed by Belgian engineer Jean Joseph Étienne Lenoir in 1858. Around 5000 engines were commercialized in sizes up to six horsepower, however, those engines had very low efficiency reaching just 5 percent [9]. Nine years later in 1867, Nicolaus August Otto (1832-1891) and Eugen Langen (1833-1895) introduced an atmospheric engine, with thermal efficiencies of up to 11% [9]. Currently, spark-ignition engines are produced based on Otto's invention.

2.1.1 Classification of engines

Internal combustion engines can be classified according to their design, application, a method of ignition or dedicated fuels. One of the most important classification types, is according to the ignition method, as mentioned in a background, there are two methods of ignition spark-ignition or compression-ignition (Diesel engines). If it comes to engine design, there are generally two designs, reciprocating engines, and rotary engines. Reciprocating engines can be divided in accordance to their configuration such as; in-line, V, radial, opposed, boxer and etc.., some of the most important commercially available configurations are presented in a Figure 6.

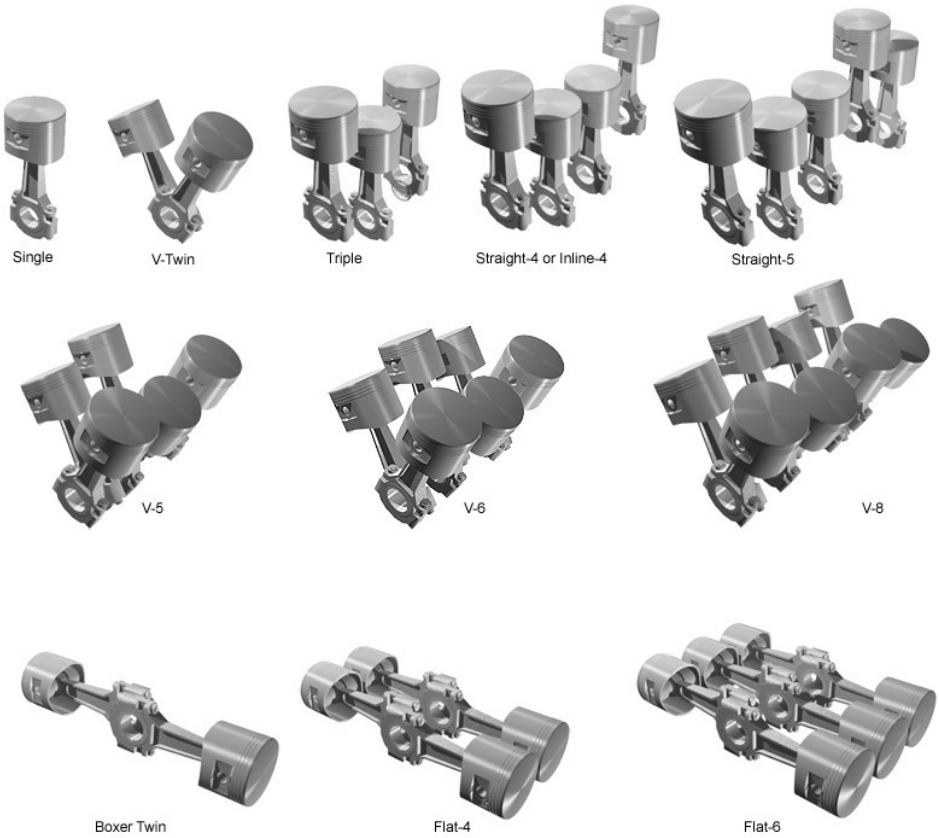


Figure 6: Reciprocating engine configurations [8].

Rotary design practiced in Wankel engine, compared to reciprocating engines, characterizes with simpler and more compact design. Additionally, it produces three power pulses per revolution, which results in higher power-to-weight ratio, greater torque output, and speed. However, this design is unfavorable in view of combustion chamber geometry, limited compression ratio, combustion proceeds with high constant pressure ratio, higher HC emissions and higher fuel and oil consumption [22]. Moreover, sealing of the combustion chamber is problematic and the design is unstable while applying as a diesel engine [22]. Combustion engines can be distinguished also due to the working cycle, two-stroke cycle or four-stroke

cycle. Comparing with aforementioned Wankel engine, two-stroke engines produce one power pulse per each revolution of a crankshaft, and four-stroke configuration produces one per two revolutions. Four-stroke configuration in comparison to the two-stroke, results in a heavier engine with more complicated design because of the valve system. Which results in higher costs and consequently higher final price of an engine. Additionally, the four-stroke configuration has lower mechanical efficiency, which is caused by a higher number of components. More sub-assemblies means higher total friction losses. However, the two-stroke configuration has lower power output because of fresh charge mixing with exhaust gases. Four-stroke conf. characterizes in lower fuel consumption and relatively complete burning of fuel, however as mentioned before due to the complicated configuration engine is bigger and requires more space and more complicated lubricating system comparing with two-stroke configuration. Notwithstanding, two-stroke configuration consumes more lubricating oil. Four-stroke engines produce less noise and moving parts last longer. Finally, the four-stroke configuration is characterized by a higher value of thermal efficiency. If it comes to application, four-stroke engines are used in cars, buses, and tracks, while, two-stroke engines in marine engines, scooters, motorcycles, mowers etc. The application is commonly known classification of engines, however, they can be also distinguished according to dedicated fuel. Those and several more options for engines classification are presented in the Figure 7.

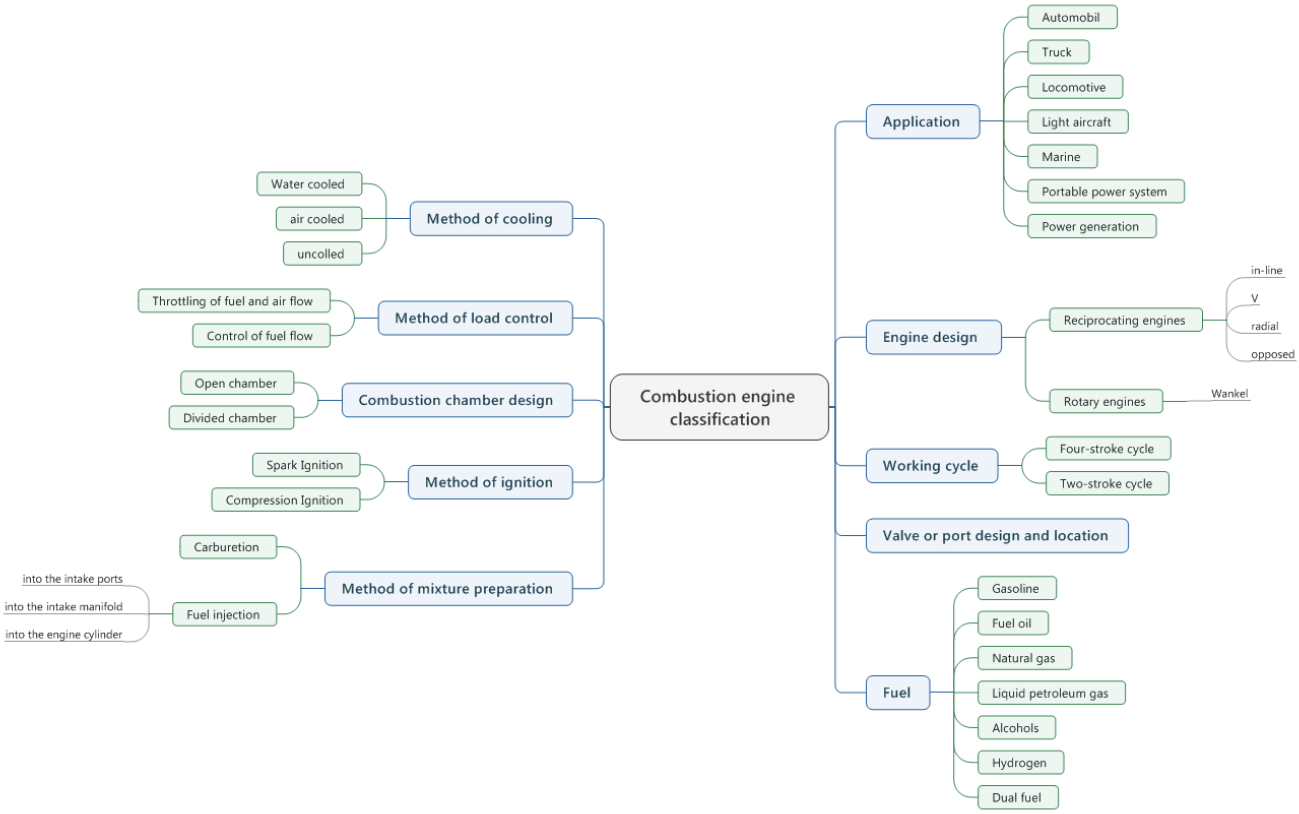


Figure 7: Classification of combustion engines. Made based on [9]

2.1.2 Operational principles

Ideal Otto cycle

Otto cycle describes the operational principles of standard spark ignition engine. The process consists of 6 stages:

- **Intake of an air-fuel mixture**, is the first step of the cycle, where air-fuel mixture is introduced into the cylinder. During this step, the exhaust valve is closed. When the process reaches step 2, presented in the figure 8 intake valve closes. It is assumed that pressure remains constant through the first process.

- **Compression**, at the beginning of this process (point 2), the piston is at bottom dead center - BDC and is going to move towards the top dead center - TDC (point 3) compressing air-fuel mixture at the same time. In an ideal Otto's cycle, it is assumed that the process is isentropic, which means that no mechanical energy is lost due to friction and no heat is transferred between the gas and surrounding. The ratio between the volume at point 6 to the volume at point 3 is so-called compression ratio.

- **Ignition and reaction** (conversion of chemical energy into thermal), this stage is presented between the points 3 and 4, the compressed air-fuel mixture in a small volume becomes ignited by a spark. Subsequently, during the combustion process, the heat inside the cylinder is growing. It is assumed that volume is constant throughout the process and piston remains in rest at TDC. However, the pressure rises significantly and the ratio between the pressure at point 3 and pressure at point 2 is called "explosion ratio".

- **Expansion (power stroke)**, points 4-5 in the Figure 8. In an ideal cycle this process is isentropic, the work is done on the piston by the system. Which means that products of combustion process - the hot gases, having high pressure are pushing the piston towards the BDC. The ratio between the volume at point 5 to the volume at point 4 is called "expansion ratio".

- **Heat rejection**, points from 5 to 6. In this stage, the volume doesn't change which means that piston stays in rest at BDC. During this process, heat is removed from the working fluid to idealized external sink, and the gas pressure drops significantly from the point 5 to point 6.

- **Exhaust stroke**, points from 6 to 1. During this process the exhaust valve is open and the piston moves from the BDC to TDC pushing out the gaseous products. After this process, the entire cycle starts again.

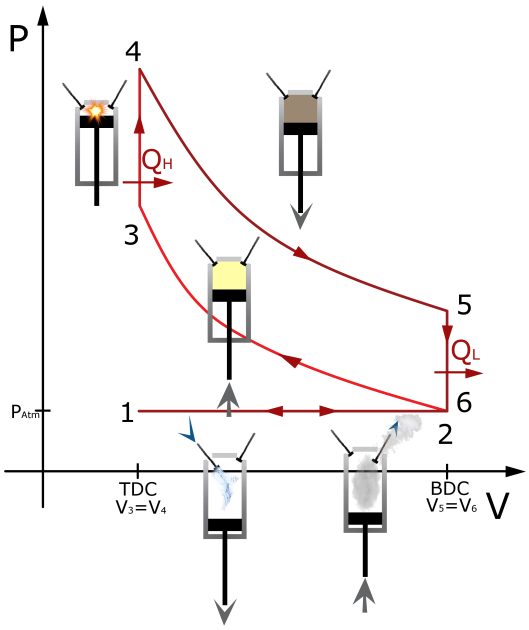


Figure 8: Ideal Otto cycle.

The ideal Otto cycle consists of two isentropic processes (first during the compression when the piston does work on the gas and second during the expansion when the gas does the work on the piston) and two isochoric processes (first one, when heat is transferred into the system and the second one, when heat is rejected from the system).

$$\eta = \frac{Work}{Heat\ input} = \frac{Q_H + Q_L}{Q_H} = 1 + \frac{Q_L}{Q_H} \tag{2.1.1}$$

Thermal efficiency η is equal to the work done by the system, divided by the heat that has been introduced into the system. Heat absorbed by the system Q_H has a positive value while heat extracted from the system Q_L has a negative value. The heat absorbed by the system is related to the temperature change from the state 3 to the state 4, this is why Q_H can be expressed in the following manner:

$$Q_H = Q_{34} = \Delta U_{34} = \int_{T_3}^{T_4} C_V dT = C_V(T_4 - T_3), \qquad W_{34} = 0 \tag{2.1.2}$$

rejected heat can be also expressed via temperature change:

$$Q_L = Q_{56} = \Delta U_{56} = C_V(T_5 - T_6) \tag{2.1.3}$$

thus, general equation for thermal efficiency, can be also expressed as a function of temperature differences:

$$\eta = 1 - \frac{T_5 - T_6}{T_4 - T_3} \tag{2.1.4}$$

As mentioned before, there are two isentropic processes, isentropic compression 2 - 3, and isentropic expansion 4 - 5:

$$T_5V_6^{\gamma-1} = T_4V_3^{\gamma-1}, T_6V_6^{\gamma-1} = T_3V_3^{\gamma-1} \tag{2.1.5}$$

$$(T_5 - T_6)V_6^{\gamma-1} = (T_4 - T_3)V_3^{\gamma-1}, \qquad V_6 = V_2 \tag{2.1.6}$$

$$\frac{(T_5 - T_6)}{(T_4 - T_3)} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \tag{2.1.7}$$

$$\gamma = \frac{C_P}{C_V} = \frac{f+2}{f} \tag{2.1.8}$$

Where;
γ - specific heat ratio (adiabatic index);
C_P - specific heat of constant pressure;
C_V - specific heat of constant volume;
f - number of degrees of freedom.

$\frac{V_2}{V_3} = r$ is so called compression ratio, thus efficiency of on ideal Otto cycle is strictly related to compression ratio, and the final form of the equation has the following form:

$$\eta_{Otto} = 1 - \frac{T_5 - T_6}{T_4 - T_3} = 1 - \frac{1}{(\frac{V_2}{V_3})^{\gamma-1}} = 1 - \frac{1}{r^{\gamma-1}} \tag{2.1.9}$$

Relation presented above has been plotted in a figure 9, for three different adiabatic indexes. Thermal efficiency is a function of compression ratio when compression increases thermal efficiency grows as well. Figure 9 includes plots of three different values of adiabatic indexes. For higher values of adiabatic indexes, thermal efficiency is greater.

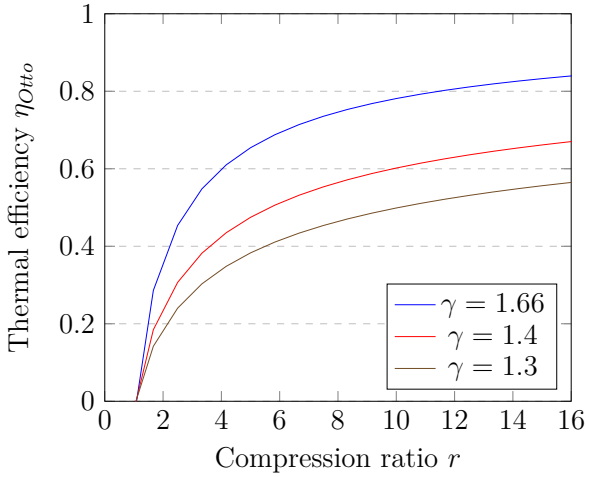


Figure 9: Relation between thermal efficiency of ideal Otto cycle and compression ratio for three different values of adiabatic indexes.

Specific heat ratio γ is the ratio of the heat capacity at constant pressure C_P to heat capacity at constant volume C_V, the ratio 1.66 is related to ideal mono-atomic gas, $\gamma = 1.4$ is related to diatomic gas for example air (78% nitrogen - N_2 and 21% oxygen O_2), at standard temperature. If it comes to value 1.3 of specific heat ratio, this is related to burned or unburned air-fuel mixture in the gasoline engine, at specified λ value and temperature (Figure 10).

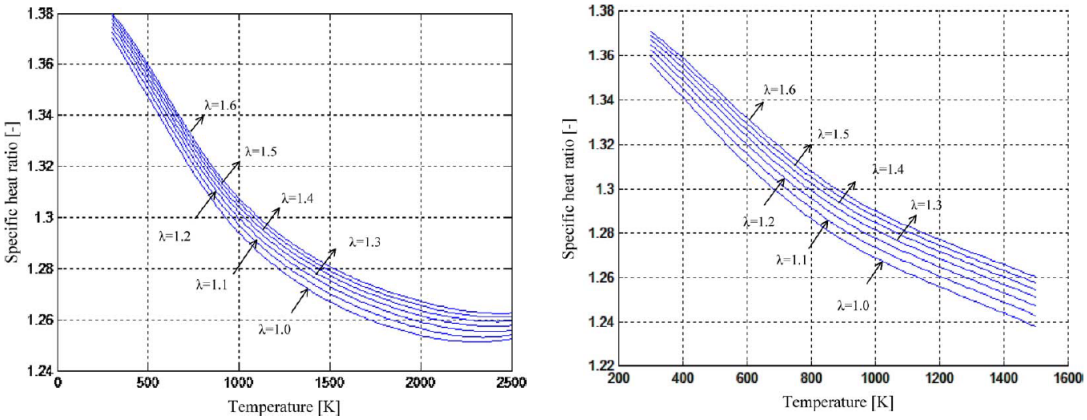


Figure 10: Adiabatic index dependence on temperature and air-fuel ratio for burned mixture left graph, and unburned mixture right graph [23].

Actual Otto Cycle

In real conditions, engine works differently than in the ideal case. Thus the pressure-volume chart of actual Otto cycle differs as well from ideal one - Figure 11.

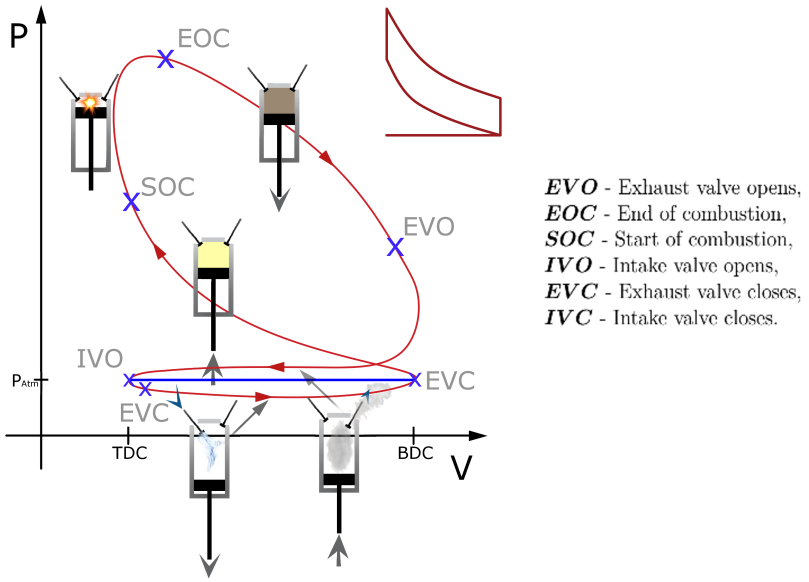


Figure 11: Actual Otto cycle with comparison to ideal one on the upper-right corner.

Actual Otto cycle has smaller work loop than an ideal one, compression stage is not isentropic, which is the effect of heat losses. To ensure the smooth operation of the piston, the cylinder is cooled and thus some portion of heat from the working fluid is transported to the walls. During combustion, the spark is fired towards the end of the compression stroke. Before combustion is finished, the piston is returning and pressure continues to rise. The power stroke is not adiabatic as well, thus more heat is lost to the surrounding. The exhaust valve opens towards the end of the expansion, therefore it should be initiated before the stroke reaches BDC. Otherwise, more work needs to be provided for lifting the piston towards the TDC. Which would result in additional power losses and consequently lower efficiency. In a pumping loop occurs so-called "pumping work" which is a negative net work. During intake, the pressure in the cylinder is lower than atmospheric, there is a partial vacuum in the intake manifold, thus work has to be done against the vacuum. On the other hand, in an exhaust stage, the pressure in the cylinder is higher than atmospheric, because the piston is pushing flue gases towards the open exhaust valve.

2.1.3 Engine operating parameters

This section is dedicated to present basic parameters and relationships that characterize engine. One of the most important parameters is compression ratio which as discussed before is related strictly to engine efficiency.

$$\epsilon = \frac{maximum\ cylinder\ volume}{minimum\ cylinder\ volume} = \frac{V_s + V_c}{V_c} \tag{2.1.10}$$

$\boldsymbol{V_s}$ so called **swept volume**, which is a volume that piston covers when moving from BDC to TDC.
$\boldsymbol{V_c}$ is called **clearance volume** or **compression volume**, which is a volume between the piston top and the cylinder top when the piston is at TDC position.

Power delivered by engine is measured by dynamometer [9], and it is a product of torque and angular speed.

$$P = 2\pi nT \tag{2.1.11}$$

$\boldsymbol{n} = \frac{\boldsymbol{number\ of\ crankshaft\ revolutions}}{\boldsymbol{Time}}$ - crankshaft rotational speed
$\boldsymbol{T}$ - Torque

$$T = Fr \tag{2.1.12}$$

$\boldsymbol{F}$ - Force
$\boldsymbol{r}$ - distance between the axis of rotation to where the linear force is applied

Work per cycle can be calculated by integration of pressure over change of volume:

$$W = \int pdV \tag{2.1.13}$$

Engine type	ε		upper limit by
	from	to	
Two-stroke SI engine	7.5	10	Autoignition
Self-injection SI engine	9	11	Knock, autoignition
SI engine Turbo	8	10	Knock, autoignition
Direct injection SI engine	11	14	Knock, autoignition
Direct injection engine Turbo	9	12	Knock, autoignition
Diesel (indirect injection)	18	24	Loss of efficiency at full load, component load, noise
Diesel (direct injection)	17	21	Loss of efficiency at full load, component load, noise

Figure 12: Minimal and maximal values of compression ratios for modern engines [21].

Subsequently, the power per cylinder can be calculated using power per cycle.

$$P = \frac{Wn}{n_R} \tag{2.1.14}$$

where, $\boldsymbol{n_R}$ is the number of crank revolutions for each power stroke per cylinder [9]. Where, four-stroke cycle has 2.

Mean piston speed measure drive of engine, and is proportional to product of crankshaft rotational speed and length of the stroke (s).

$$c_m = 2 \cdot s \cdot n \tag{2.1.15}$$

However, more important is a **maximal piston speed**, which is indicating the maximal value of piston speed, that is acceptable for safe operation of an engine. When the piston speed is higher than internal forces, wear and friction increase as well, thus designed c_{max} shouldn't be exceeded.

Brake mean effective pressure (p_{me}) represents the capacity of engines to do work, and is independent from engine displacement [9]. Engines with higher values are more powerful and efficient.

$$p_{me} = \frac{Pn_R}{V_s n} \tag{2.1.16}$$

Specific fuel consumption measures how efficiently engine uses the fuel to produce work [9].

$$b_e = \frac{\dot{m}_f}{P_e} \tag{2.1.17}$$

Engine type	Maximum speed (rpm) approximately	Mean piston speed (m/s) approximately
Racing engine (Formula 1)	18,000	25
Small engines (two-stroke)	20,000	19
Motorcycle engines	13,500	19
Car SI engine	7500	20
Car diesel engines	5000	15
Truck diesel engines	2800	14
Larger high-speed diesel engines	2200	12
Medium high-speed engines (diesel)	1200	10
Crosshead engines (two-stroke diesel)	150	8

Figure 13: Mean and maximal piston speed for different engines [21].

$\boldsymbol{P_e}$ - brake power.
$\boldsymbol{\dot{m}_f}$ - fuel mass flow [kg/s].
sfc, helps to calculate fuel conversion efficiency:

$$\eta_f = \frac{1}{sfcQ_{HV}} \tag{2.1.18}$$

Volumetric efficiency is a measure of effectiveness of an engine's induction process [9]. In other words volumetric efficiency measures engine's ability to breathe freely. The easier the air flows to the piston, the greater its volumetric efficiency and power output.

$$\eta_v = \frac{2\,\dot{m}_a}{\rho_a V_s n} = \frac{m_a}{\rho_a V_s} \tag{2.1.19}$$

$\boldsymbol{\dot{m}_a}$ - mass flow of air,
$\boldsymbol{\rho_a}$ - intake air density.

Specific emissions can be calculated through dividing mass flow of each component by power output.

$$s_i = \frac{m_i}{P_{out}} \tag{2.1.20}$$

$\boldsymbol{i}$ is a component such as NO_x, CO, HC etc...

2.1.4 Engine efficiency

Each fuel has specific chemical energy contained in bonds between the atoms. The engine converts the chemical energy of a fuel into mechanical energy in a form of a

drive. This conversion is strictly related to a chain of losses occurring during the diverse processes. As presented in an Ideal Otto Cycle section, the thermal efficiency of a cycle is less than 100% which is related to the thermodynamic losses during the ideal process. There are several ways, that can increase an efficiency of a cycle, for example increasing compression of the air-fuel mixture. In the p-V diagram, it manifests as a larger enclosed area [11]. However, while increasing compression ratio, anti-knock properties of fuels need to be taken into the consideration [11] (this issue is discussed more specifically in following chapters 2.2.1). Thermal losses in the cylinder are also of high importance, as mentioned in an actual Otto cycle section, part of the heat passes to the surrounding via cylinder walls. Other thermal losses result from the residual heat of the exhaust gases. Additionally, there occur losses due to the stoichiometric combustion (λ=1), the best efficiency according to experience is obtained for $1.1 < \lambda > 1.3$ [11]. However, when the 3-way catalytic converter is applied, λ value has to be kept constant: 1. This is required for proper operation of oxidation and reduction processes. In an actual Otto's cycle - Figure 11, exhaust stroke line is above atmospheric pressure (pumping loop), which is connected with further losses because piston has to perform additional work to push out the exhaust gases. On the other hand, there is a vacuum in an intake manifold, which produces "throttling losses" [11] during the intake stroke. Those two effects together are called "pumping losses". Apart from the aforementioned losses, there are frictional losses, produced by piston-rings at the cylinder walls, the bearing friction or the friction of the alternator drive [11]. In conclusion, effective power output is just 28.5% of the total energy stored in the fuel. Figure 14 presents above discussed losses.

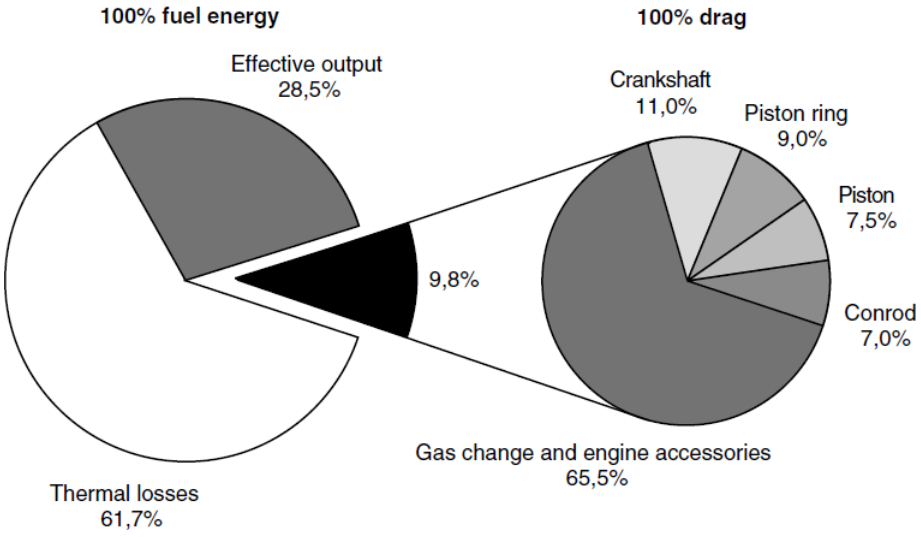


Figure 14: SI engine efficiency classification [21].

Brake thermal efficiency (η_e) represent overall performance of an engine, taking into account all discussed losses..

$$\eta_e = \eta_t h \cdot \eta_a \cdot \eta_b \cdot \eta_m = \eta_i \cdot \eta_m \tag{2.1.21}$$

where, η_i is so called indicated efficiency

Brake thermal efficiency can be also calculated as a quotient of effective power by product of fuel mass flow and its net calorific value.

$$\eta_e = \frac{P_e}{\dot{m}_f \cdot H_f} \tag{2.1.22}$$

Thus, indicated efficiency can be also expresses similarly:

$$\eta_i = \frac{P_i}{\dot{m}_f \cdot H_f} = \frac{i \cdot n \cdot p_{mi} \cdot V_h \cdot z}{\dot{m}_f \cdot H_f} = \frac{i \cdot n \cdot p_{mi} \cdot V_H}{\dot{m}_f \cdot H_f} \tag{2.1.23}$$

P_e - brake power
i - working cycles per revolution (for four-stroke engines: i=0.5 and for two-stroke engines: i=1).
P_{mi} - indicated mean pressure.
V_h - piston displacement, which is a distance that piston travels during single piston stroke from BDC to TDC.

$$V_h = \frac{\pi \cdot d_K^2}{4} \cdot s \tag{2.1.24}$$

s - piston stroke,
d_K - piston diameter,
V_H - total displacement of the engine,

$$V_H = V_h \cdot z \tag{2.1.25}$$

z - number of cylinders

2.1.5 Engine components

This chapter is focused on engine components, functions that they perform in SI engine and materials that have been used to produce them. The most important basic parts of the engine are cylinder block, cylinder head, pistons, piston rings, connecting rod, crankshaft and crankcase, engine bearing, valves, spark plug, manifold, camshaft and piston pin. Cylinder block forms the main body of an engine, it includes combustion chambers and guides the pistons. Important structures are oil and water channels that ensure circulation of those fluids, providing appropriate lubrication and cooling. Generally, cylinder blocks are made by the high quality cast iron which is characterized by good wear resistance and low cost. Cylinder head made of cast iron or aluminum is sealing the cylinder block. It makes the top part of the combustion chamber, where all intake and exhaust valves are located and optionally spark plugs (SI engines). Pistons, most commonly made of aluminum are receiving gas pressure and transmitting the thrust to the connecting rod. Piston rings are produced from cast iron. They are sealing pistons and cylinders, where additionally decreasing

friction between them and preventing fuel and lubricating oil leakages. Connecting rods are made of nickel, chrome and chrome vanadium steels or aluminum. They transmit the reciprocating motion of the pistons into rotary motion of the crankshaft. Crankshafts are produced from steel forging or nodular cast iron. Engine bearings are commonly made of steel and they support moving parts of an engine. The crankcase is produced from cast iron or cast aluminum, it serves as a cover to which all cylinders are attached and contains the crankshaft with its bearing. Additionally, the crankcase is storing lubricating oil. Valves are made of stainless steel, and they control the inlet and exhaust of an engine. In the case of spark ignition engines, there are spark plugs that are producing a necessary spark for initiation of the combustion process. The manifold made of aluminum alloy has two functions: supplying air-fuel mixture and collecting the exhaust gases. The camshaft is produced from chilled iron castings and is controlling the opening and closing of intake and exhaust valves at right sequence and duration. The piston pin is made of hardened steel and the main function is connecting piston bosses with connecting rods and connecting rods with swivel.

2.1.6 Injection systems and mixture formation

Fuel injection method is very important and influences on combustion and general efficiency of an engine. Injection can be divided into **single point injection** (figure 15, point a) or **mluti-point injection**. Multi-point injection (figure 15, point b, and c), subsequently can be divided into the three further options, direct (figure 15, point c), indirect (so-called port or manifold injection) (figure 15, point b) or "dual injection". **Indirect injection** ia a process when the fuel is introduced into the intake manifold, where mixes with air and later introduces into the intake manifold. Another, more efficient process which leads to greater power output and fuel efficiency is called **direct injection**. This system was originally designed for diesel engines, however, currently, direct injection is applied in gasoline engines as well.

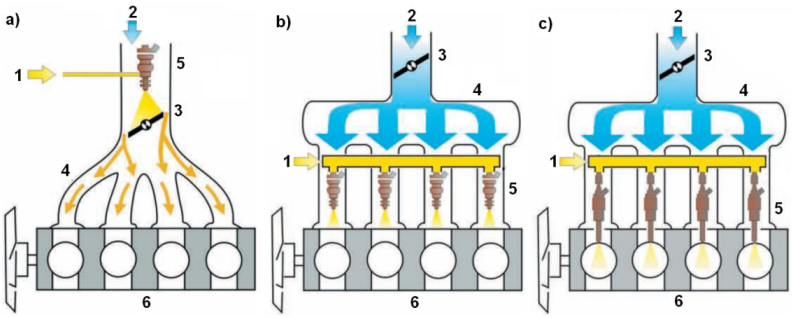


Figure 15: Fuel injection systems, a -single point injection, b - multi-point port injection, c - multipoint direct injection [15].

Port injection

Indirect injection system introduces fuel into the intake manifold or intake passage, where the air/fuel mixture is formed. The process starts with the pumping of a

fuel by an electric pump to the fuel injectors, under system pressure. A subsequent process called mixture formation aims to supply a highly homogeneous fuel vapor and air mixture into the combustion chamber and ensure a good ignition. The air-fuel mixture, should also have a good dynamic behavior in a non-stationary operation and emit low amounts of hydrocarbons during cold start [11]. Mixture formation stage is sensitive to engine temperature, primary-droplet spray, the instant of injection, spray targeting and air flow. The fuel spray, straight after exiting from the injector is called *primary-droplet spray*. In the cold engine conditions, a small portion of the fuel evaporates in the intake manifold, thus fuel tends to create so-called "wall-applied film" [11]. Subsequently, it enters to air during the intake process, and form a mixture in a cylinder. However, in the hot engine conditions (in the intake manifold), a significant portion of the injected fuel and "wall-applied film" evaporates. As mentioned before the instant of injection, plays a very important role, especially if it comes to HC emissions in cold engine conditions. There are two modes of injection, intake-synchronous injection and pre-intake injection. During the first process, injection proceeds when the intake valve is open, this leads to agglomeration of the fuel in the wall by the exhaust valve which subsequently forms a film on the wall. This phenomenon causes troubles during the cold engine conditions, due to the fact that, this fuel film doesn't evaporate easily, which in consequents remains after combustion. As a result, unburned fuel passes to the exhaust port and increases emissions of HC. On the other hand, this process increases engine power, when running at regular hot conditions. The positive phenomenon is related to cooling of cylinder walls, by fuel evaporation in the combustion chamber, which in effect reduces engine knock [11]. If it comes to hydrocarbons, the process of pre-intake injection helps to reduce emissions during cold start. There is a possibility to decrease emissions of HC even further through the spray targeting. If the spray is concentrated more towards the intake port than towards the exhaust port, it will result in a reduction of fuel film formation on the cylinder wall. Mixture formation is a process that is highly dependent on air flow, which is subsequently controlled by engine speed, and dependent on the geometric layout of the intake port, opening time and life curve of the intake valves [11]. Airflow has to be adjusted enough much, to deliver necessary air at the right time to the combustion chamber. Strong air-flow increases homogenization of the mixture [11]. Extremely important is a manifold pressure, when it is higher than the pressure in the cylinder, air-fuel mixture and "well-applied" film are pushed into the combustion chamber. Whereas, in opposite situation, hot exhaust gases from the previous combustion will flow to the intake manifold. Additionally, lower pressure in the manifold causes so-called pumping losses.

Direct injection

Direct injection (DI) means an injection of fuel directly into the combustion chamber at high pressures. There are two pumps that are helping to reach necessary pressure: electric pump located in a tank which is pumping the fuel with a pressure of 3-5 bars [11], and high-pressure pump situated before the fuel rail. HP pump generates

the pressure that is suited to the requested torque and engine speed [11]. In the DI systems, there is internal mixture formation, which simply means that air-fuel mixture formation takes place inside the combustion chamber [11]. In this method, combustion chamber design, intake manifold, injection point geometries and the moment of ignition are decisive if it comes to mixture formation and fuel conversion performance. The essential parameter that ensures high-quality combustion is a relation between injected fuel and air-flow. Generally, there are distinguished two combustion processes, stratified-charge and homogeneous combustion process.Homogeneous combustion process require stoichiometric conditions $\lambda = 1$, which results in lower emissions of NO_x. The second one called stratified-charge combustion dominates in regions of small load and low engine speed [11]. Fuel is injected during the compression stroke, into the combustion chamber and becomes "wall guided" to the spark plug, whereas air in conditions of $\lambda > 1$, fills remaining space of the cylinder. Stratified-charge combustion allows operating unthrottled in greater ranges, which results in reduced pumping losses and better efficiency. There are two concepts, wall/air-guided process and spray spray-guided process [11]. In the first concept, injection proceeds between 50 to 150 bar, and then the mixture is led by the piston recess shapes [11].Whereas, air flow can be adjusted, and introduced under different angles in order to obtain better mixing. Airflow can be introduced even as a swirl or tumble flow. During the swirl flow, the air generates a turbulent flow, whereas the second process produces a tumbling flow [11]. Important is the fact that both processes are wall-guided. Another type is a spray-guided process, where the injector is located at the central-top of the combustion chamber's roof. As mentioned before, during this process fuel spray is guided directly to the spark plug which is located next to the injector. This effect is advantageous due to the fact that it allows to avoid circuitous routes through the piston or air flows [11]. However, there is an issue regarded to the short amount of time that is available for mixture preparation. One of the possibilities that solve this effect is to increase the pressure of injection, to about 200 bar [11]. Another disadvantage is that spark plugs are exposed to significant thermal stresses when they are hot and exposed to the cold jet of injected fuel [11]. In comparison to "wall/air-guided" process, stratified-charge process represent greater efficiency and thus fuel consumption savings [11]. Mixture formation in a case of a homogeneous process should be homogeneous through the entire combustion chamber whereas in stratified-charge processes only within a specified area. Injected fuel has to evaporate before homogenization, there are some parameters that are limiting this process, such as combustion chamber temperature, fuel-droplet size or available time for evaporation [11]. The air-fuel mixture has to meet some criteria to be classified as a combustible, one of this is a λ parameter which for gasoline has to be kept between 0.6 and 1.6. Another is a temperature, which has a decisive influence for evaporation, if it is too low, fuel will not evaporate sufficiently, and as a result, more fuel has to be provided in order to maintain the combustible nature of a mixture. Injection pressure regulates droplet sizes, that are smaller at higher pressures. However, when the pressure of injection increases, it will increase also so-called "penetration depth" [11], which is a distance that the fuel droplet travels before complete evaporation. Thus, if the "penetration depth" is higher than the

distance from the injector to the combustion chamber wall, it will contribute to the fuel film formation on the walls [11]. Which results in incomplete combustion and growth of HC emissions. In a homogeneous mode, fuel should be introduced to the combustion chamber as early as possible, to increase the time needed for mixture formation [11]. The intake of air should be at high velocities, to maintain support of faster fuel evaporation and increase homogenization. In a stratified-charge mode fuel is injected during the compression stroke, to ensure that the mixture cloud will be transported towards the spark plug. Transport of mixture is indicated by air flows and upwards movement of the piston [11]. In this mode, the injection point is adjusted to the engine speed and torque [11]. Higher temperature and pressure in the combustion chamber are advantageous in this mode from the mixture preparation point of view [11]. Unfortunately, during the process of "wall-guided" combustion, fuel film formation on the piston wall is a challenging effect.

Dual injection system

Dual injection systems consist both of direct fuel injector and port fuel injector. This process characterizes in better distribution of the air-fuel ratio within the volume of cylinder comparing to separate cases of port injection and direct injection [15]. Another advantage is a high quality of a homogeneity of the mixture, which results in significantly improved combustion and greater fuel effectiveness.

Injectors.

The fuel injector is a device responsible for introducing fuel into the combustion chamber in a right time, right amount and at the appropriate pressure. Depending on fuel injection system, whether it is direct or indirect injection, there are different injector designs. If it comes to direct injectors, they provide higher fuel pressure and significantly shorter injection time. Gasoline direct injection enhances a homogeneous and lean-burn combustion, it provides exact flow and enhances engine performance comparing with manifold injection. The electro-hydraulic servo valve is an electrically controlled valve, that transforms changing analog or digital input signal into a movement in a hydraulic cylinder. The advantage of this system is precise control of piston and velocity. Additionally, this system is controlled by a low voltage. Piezo actuator as a core part of injector creates a possibility for low electrical voltages and meets the automotive requirements related to temperature and vibration [21]. It opens and closes the servo valve in less than 100 μs [21]. Servo valve and harmonized input and output throttle combination to the control area (which is above the nozzle needle) control the nozzle opening speed [21]. Thus minimal injected fuel quantity is also controlled via minimum operating time. Piezostack has to be isolated from the surroundings temperature influence, due to the fact that engine operating temperatures have a wide range, and can affect the duration of the injection. When the injector is open too long, more fuel becomes introduced to the combustion chamber, and this can lead towards engine damages [21]. In reverse situation, during short operating times, the injector cannot remain closed. This results in absence of the pre-injection (pilot injection), which softens the main injection pressure rise

and reduces combustion noise. This kind of injector can operate over the entire range of engine temperatures from $-30°C$ to $+140°C$, maintaining control valve lift of approximately $40\mu m$ [21]. When the rail-piezo injector is not operating, the nozzle needle is pressing the injection orifices and covering them at the same time. During operation, nozzle needle becomes pulled upwards and uncovers the injection orifices. After that fuel stored at high pressure passes through the injection holes to the combustion chamber. When the injection orifices are closed, fuel is stored at high pressure in injector control area and at the high-pressure chamber located at the nozzle [21]. There are two different hydraulic forces, one F1 which acts on the control piston and second F2 acting on the nozzle needle, and in this case, F1 is greater than F2, which ensures that the nozzle of the injector is closed [21]. When the piezo actuator is controlled, it presses the valve plunger and opens the hole which is connecting the control area with the fuel-return [21]. As fuel returns decrease pressure at control area and F2 becomes greater than F1. When this happens, nozzle needle is forced to become pulled upwards, and fuel is injected. Additionally, the design of the injector nozzle is very significant. Parameters such as injector seat, nozzle hole size, and shape affect combustion characteristics, emissions, engine performance and mechanical durability of the injector. Subsequently, an indication of the exact amount of the fuel that has to be injected is extremely important. There are several factors that must be considered during determination, such as smoke limit, maximum permissible cylinder pressure, exhaust gas temperature, engine revolutions, torque, and revolution upper limits [21]. Equation 2.1.26 helps to calculate appropriate injection volume per work cycle and cylinder. That eq. is adjusted to the four-stroke engine.

$$V_K = \frac{P_e b_e 2}{z n_m \rho_K} \tag{2.1.26}$$

P_e - effective performance of the engine,
b_e - specific fuel consumption of the engine [mass/performance and time],
z - number of cylinders,
n_M - engine speed,
ρ_K - fuel density.

However, there exist issues related to pre-delivery, post-delivery, delivery during operation and closing of the injector, that are not included in equations 2.1.26. Thus equation 2.1.27 includes those effects and represents the fuel column exiting the nozzle [21].

$$V_{Off} = A_D \cdot \Delta t \cdot \alpha \sqrt{\frac{2}{\rho_K} \Delta p} \tag{2.1.27}$$

A_D - geometrical nozzle-hole cross section,
Δt - injection time,
α - through flow rate,
Δp - differential pressure (fuel-side to combustion-side) [21].

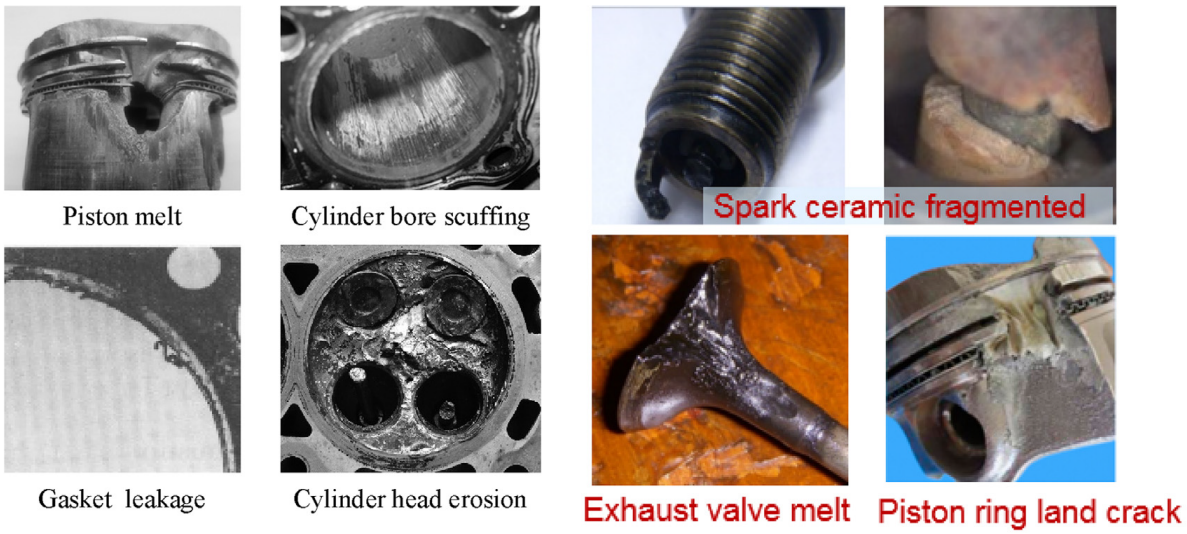
2.2 Combustion process and related issues

Combustion is a chemical reaction of fuel oxidation, during this process energy stored in an atomic bonds of fuel molecule is converted into thermal energy in the form of high-temperature gases and some small amount of losses in a form of electromagnetic energy (light), electric energy (free ions and electrons) and mechanical energy in a form of a noise [28]. The internal combustion engine is supplied by oxygen from the air, which consists mainly of nitrogen (78%) and just 20.9% oxygen (1% - other gases). American company TruTechTools, that produces combustion and emission testing equipment, wrote on their website that combustion efficiency is not able to overcome 95% for most fuels as long as air is used as oxidizer medium in the process. This effect is the result of a nitrogen presence, which cools down the burning temperature [27]. Fuels contain different compounds, however mainly - hydrocarbons, during real combustion, fuel is converted into CO_2, H_2O, a small amount of CO, gases, liquid or solid aerosols, a trace amount of SO_2 or SO_3, ash and inert gases. Combustion can be complete or incomplete. **Complete combustion** is characterized by the conversion of entire hydrogen and carbon into water and carbon dioxide. Theoretically, during stoichiometric conditions, there should be no oxygen, excess air or carbon monoxide in the flue gases. However, in reality, limitations such as not perfect mixing and finite reaction rates, make the model just impossible. Thus, fuel should be combusted in excess air conditions in order to ensure complete combustion. **Incomplete combustion** is a result of incomplete oxidation of a fuel. This process leads to carbon monoxide, aldehyde and ketone emission. Incomplete combustion can occur when there is not enough air supplied to the combustion chamber, poor fuel mixing, insufficient air supply to the flame, insufficient reactant residence time in the flame, flame contact with the cold surface and too low flame temperature [28]. As a result of incomplete combustion, fuel is consumed inefficiently and hazardous gazes are released into the atmosphere.

2.2.1 knocking combustion

The automotive industry is following the direction towards more efficient engines that are producing fewer emissions. Spark ignition engines show a huge potential to meet the EU goals, however, there is one big obstacle to overcome - knocking combustion. When the air-fuel mixture in the end- gas region is sufficiently compressed and reaches high enough pressure and temperature, there can occur process called auto-ignition (ignition not caused by spark plug). As a result, a shock wave is generated which creates the metallic “pinging” sound, and at the same time, cylinder pressure increases significantly. The most desirable scenario is when ignition occurs in precise point in the piston stroke, initiated only by the spark plug. Knocking combustion results in various damages, for example, piston crown melting, piston ring sticking, cylinder bore scuffing piston ring-land cracking cylinder head gasket leakage and cylinder head erosion [16]. Producers are continuously improving engines power density, decreasing fuel consumption and emissions, mainly by applying high boost and direct injection. Whereby, a new mode of knocking called super-knock has been discovered. Conventional knocking combustion decreases thermal efficiency by

limiting the rise of compression ratio because of end-gas (the last part of the air-fuel mixture which is set into the cylinder, however, is not yet consumed in the normal flame-front reaction) auto-ignition. Whereas super-knock because of detonation is limiting the boost, which improves the power density of modern SI engines [16].



a) Conventional knock (adapted from [1]) b) Super-knock (Reprinted from [2] with permission of SAGE)

Figure 16: Destruction caused by conventional knock and "super-knock" [16].

2.2.2 Conventional Knocking combustion

Knocking results from the end-gas auto-ignition towards propagating flame. This process consists of two stages: flame propagation initiated by spark ignition and end-gas auto-ignition which results in pressure oscillation [16]. The flame propagation stage starts with spark ignition and ends with the beginning of pressure oscillation. Figure 17 presents the process, and there is short pressure drop, which is related to the downward movement of the piston and heat transfer. Unburned gas temperature increases without oscillations because of two reasons: firstly compression heating effect of the burned gas and propagating flame, secondly compression or expansion caused by the moving piston [16]. Before the beginning of auto-ignition stage, pressure and temperature of end-gas are reaching high values and initiating auto-ignition, when this happened a pressure wave propagates into the chamber, and is reflecting back and forth from the walls, resulting in pressure oscillations. In the beginning, pressure increases significantly reaching peak value, and after that, pressure oscillates with decreasing trend.

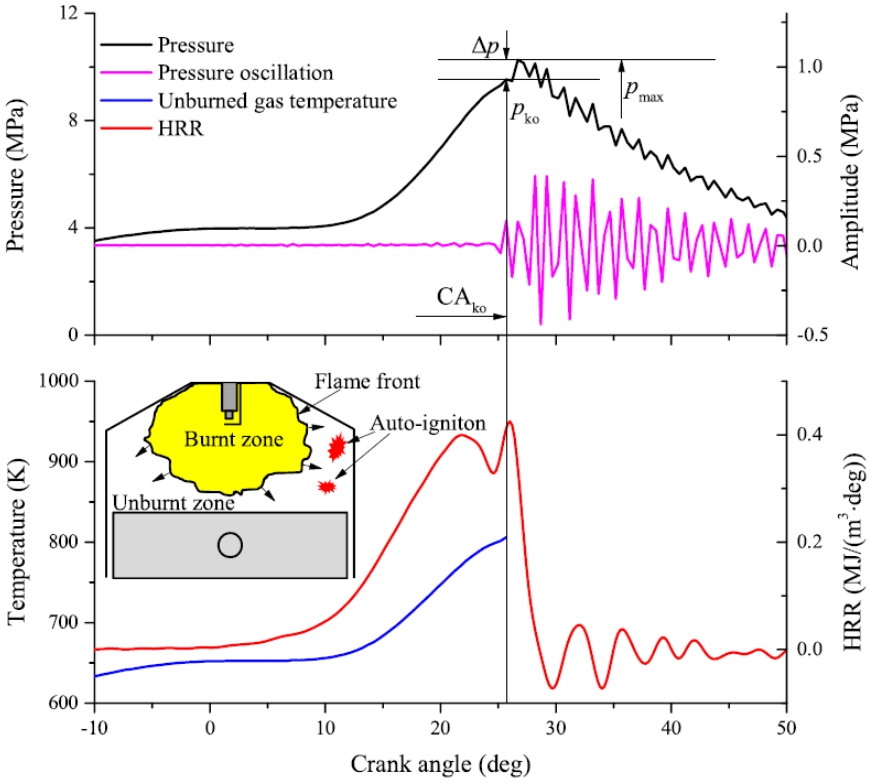


Figure 17: Knocking behaviour [16].

There are several important parameters that are helping to characterize knocking behavior.

- Heat release rate:

$$\dot{Q} = \left(\frac{\gamma}{(\gamma-1)}\right) P \frac{dV}{d\theta} + \left(\frac{1}{(\gamma-1)}\right) V \frac{dP}{d\theta} \tag{2.2.1}$$

ΔP - maximum pressure rise,
γ - specific heat ratio,
θ - crank angle,

- Temperature of the unburned gas (T-unburned):

$$\int_{T_0}^{T(t)} \frac{\gamma}{(\gamma-1)} d(ln\, T) = ln \frac{p(t)}{p_0} \tag{2.2.2}$$

- Knock Intensity (KI)

$$KI = \int |p_{HPF}| d\theta \tag{2.2.3}$$

P_{HPF} - high-pass filtering

2.2.3 "Super-knock"

"Super-knock" is a new type of knocking combustion, which manifests itself in significantly stronger peak pressure and pressure oscillations (figure 18), that is very dangerous for the engine. This effect can be observed particularly in the low-speed and high-load regime at modern SI engines with turbo-chargers [16]. The "super-knock" phenomena is a major issue if it comes to boost level improvements in turbo-charged SI engines because standard methods for knock decreasing are not effective in this case. Techniques include: retarding spark timing, cooling the intake charge, and enhancing heat transfer [16].

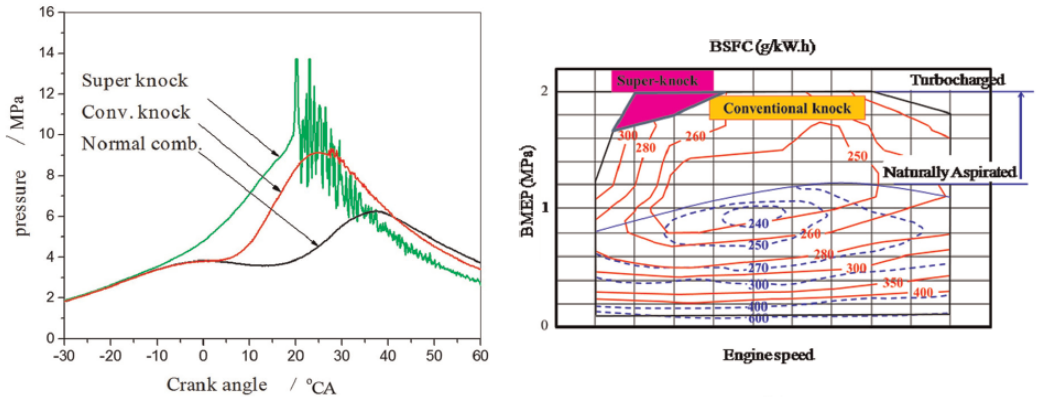


Figure 18: Comparison of normal combustion, conventional knocking and "super-knock" [29].

Figure 18 presents the difference between normal combustion, conventional knock and super-knock cycle. The amplitude of the maximum pressure rise for the super-knock cycle is much higher than for conventional knocking. The "super-knock" cycle results similar to conventional knocking from "pre-ignition", which is an ignition caused by a source other than the electric spark, and before the spark time [29]. However, the difference is that conventional knocking is related to end-gas auto-ignition, while "super-knock" arises from sporadic pre-ignitions, that are causing much stronger knock effect and engine damage (Figure 18).

2.2.4 Knock resistance - octane number

There is a measure, which describes knock resistance of a fuel called Octane Index, Octane Number (ON) or Control Octane Number (CON). In order to properly describe knocking resistance, the Research Octane Number (RON) and Motor Octane Number (MON) were applied to SI fuels. Figure 19 represents Waukesha CFR Octane Rating Unit, where RON and MON measurements are carried out for different fuels on a single-cylinder SI engine.

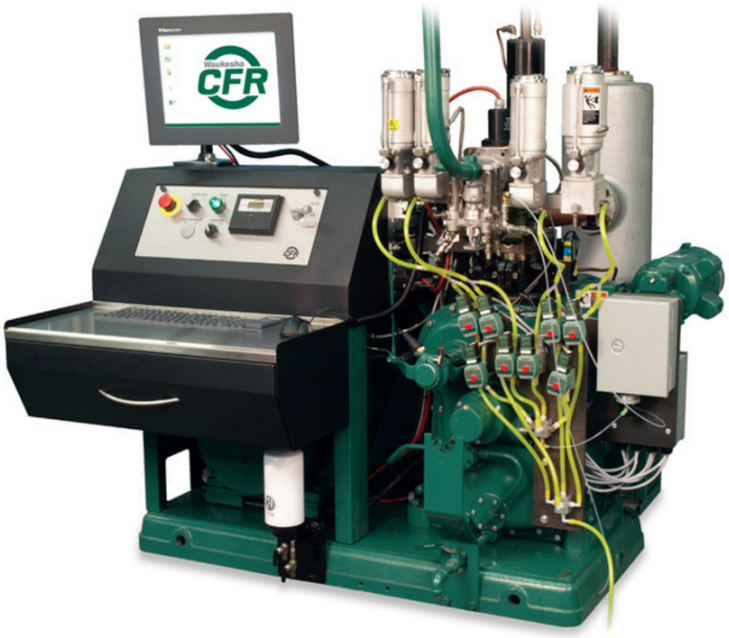


Figure 19: Waukesha CFR Octane Rating Unit [31].

The RON and MON methods are testing particular fuel or blend of fuels under conditions presented in a table 2.

Parameter	RON	MON
Intake air temperature	$52°C$	$149°C$
Intake air pressure	atmospheric	atmospheric
Coolant temperature	$100°C$	$100°C$
Engine speed	600 rpm	900 rpm
Spark timing	$13°bTDC$	$14-26°bTDC$
Compression ratio	4-18	4-18

Table 2: Operating conditions of RON and MON [16].

In general, RON represents mild driving conditions and is no consistent with heavy loads. RON is a better indicator for engines operating at full throttle and low engine speed, whereas MON represents severe, high speed and high load driving. MON is better for engines operating at full throttle and high speeds or part throttle, low and high engine speeds [16]. Motor octane number is tested in European filling stations. During the tests, a mix of iso-octane with assigned octane rating equal 100 and n-heptane with octane rating equal 0 is used as a Primary Reference Fuels (PRF). The purpose of the test is to find the mix of iso-octane and n-heptane that behaves identically to the fuel that is tested. When the mix matches the fuel that was examined, octane number can be indicated for that fuel. A very important parameter is fuel sensitivity (S) which is a difference between RON and MON.

$$S = RON - MON \tag{2.2.4}$$

Generally octane index (AKI - antiknock index) is calculated as a (ROM+MON)/2.

$$AKI = \frac{RON + MON}{2} \tag{2.2.5}$$

The knock resistance of a fuel is associated with an engine in which is used and operating conditions. When octane index of the fuel is lower than required by the engine, the knock will occur. Additionally, RON and MON also characterize heat of vaporization of the fuel.

2.2.5 Knock resistance enhancement

Pure gasoline has limited knock resistance, thus refineries, are mixing gasoline with different additional components in order to enhance the resistance of the fuel. Mainly, components containing oxygen produce good results and increase the octane number of a fuel. One of the main groups are Ethers such as MTBE (methyl tertiary butyl ether) or ETBE (ethyl tertiary butyl ether). Another group is represented by alcohols, mainly methanol and ethanol. On the one hand addition of alcohols increase octane number, but on the other hand, it produces a chain of difficulties, such as increased volatility, which can lead to damages (elastomer swelling, corrosion) and operational abnormalities of fuel injection system.

2.3 Fuel characteristics

Fuels are designed for energy production purposed, there can be different forms such as heat, electricity or mechanical power. Dependent on the type of fuel they release its energy either through a chemical reaction for example combustion or nuclear reaction like fission or fusion. Fuels can be in solid, liquid or gaseous form. However, for internal combustion engines, there are usually applied liquid or gaseous phases. Fuels can be produced from renewable feedstock such as biomass or fossil feedstock (so-called fossil fuels). Fossil fuels are extracted from petroleum or crude oil, which was formed millions of years ago from the remnants of decaying organisms [11]. Both renewable and fossil fuels are made of hydrocarbons, however, the quality of the fuel plays an essential role from the proper vehicle operation point of view and low exhaust-gas emissions. Spark ignition engine uses generally gasoline, which is composed of paraffin and aromatics. However, for increasing fuel's quality and optimizing properties they are mixed with fuel oxygenates such as ethanol and different additives. Gasoline contains mainly:

- **Standard paraffin** (alkanes) are described by a general formula C_nH_{2n+2}, the carbon atoms in paraffins are joined by a single bond. Paraffins are produced during the process called cracking, from the lipid feedstock. Alkanes that have less than five atoms of carbon (n<5) in standard conditions of pressure and temperature are present in a gaseous phase. Where, alkanes with less than 17 atoms of carbon at the same conditions occur in liquid phase, if their n>17, they are in a solid phase.

- **Iso-paraffins**, when alkanes have more than three atoms of carbon, they can be arranged in many different ways, and they are so-called structural isomers. The flagship example is a normal octane (n-octane) and isomer - isooctane (2,2,4-trimethylpentane), this isomer the most commonly used one. However, there are 17 more structural isomers, or 23 more if stereo-isomers included. Isomers are more stable, thus they increase properties of a fuel, such as knocking resistance.

- **Alkens** also knowns as olefins, have at least one double bond between the carbon atoms in comparison to paraffins. They are described by a formula C_nH_{2n}. Olefins are usually stable components, have higher octane numbers than paraffins and are more reactive. Similarly to paraffins they also have isomers. They are characterized by clean-burning, they decrease VOC (Volatile Organic Compound). However, increase NMOG (Nonmethane Organic Gas) [20]. This compounds during partial oxidation and oligomerization produce high-viscosity, high-molecular-weight materials known as a gums [19]. Gums can contribute to many undesirable effects such as fouling the intake manifold, blocking fuel pump membranes, nozzles, and fuel injectors. Where in the worst case it can cause sticking of piston rings. Another forms are diens, they are basically olefins with more than one double bond between the carbons. They are usually unstable, characterized by significantly higher reactivity, toxicity, and air-reactivity [20]. This component should have concentrations way bellow 1% in the fuel.

- **Aromatics**, are chemical components - hydrocarbons formed in a circle, they have a de-localized pi electron between the carbon atoms. Generally, aromatics are very stable and have high octane numbers, but on the other hand, they have very serious disadvantages. Aromatics are proven to be carcinogens, which means that exposure to aromatic compounds, through inhalation or skin contact can cause cancer. Another negative fact is that aromatics during combustion, are forming a soot [19]. Because of those issues, aromatic content is limited to maximum 35%(V/V). However, benzene is treated separately, due to the fact that is a carcinogen that can lead to leukemia [19]. Benzene content, thus shouldn't exceed a concentration of 1% in volume bases [17].

- **Naphthalenes**, belong to polycyclic aromatic hydrocarbon (PAH) branch. The simplest form, naphthalene has formula $C_{10}H_8$, its structure consists of connected to each other two rings of benzene. Naphthalenes are heavier aromatic compounds and similarly, their aromatic bond is distributed evenly around the rings. Naphthalenes are responsible for the formation of soot and smoke, which is harmful effect for SI engines.

Additionally, Figure 20 summarizes the most relevant compounds of gasoline including heir research octane number (RON).

Compound	Research octane number	Compound	Research octane number
C_4 compounds		***C_7 compounds, cont'd.***	
n-Butane	93	Methylcyclohexane	75
C_5 compounds		2,2-Dimethylpentane	93
n-Pentane	62	2,2,3-Trimethylbutane	113
1-Pentene	91	Toluene	124
2-Methyl-2-butene	97	***C_8 compounds***	
2-Methylbutane	99	2-Methylheptane	23
2,2-Dimethylpropane	100	Ethylcyclohexane	43
Cyclopentane	101	1.3-Dimethylcyclohexane	67
C_6 compounds		1,4-Dimethylcyclohexane	68
n-Hexane	25	2,3-Dimethylhexane	71
2-Methylpentane	73	1,2-Dimethylcyclohexane	81
3-Methyl-2-pentene	78	2,2,4-Trimethylpentane	100
Cyclohexane	83	2,2,4-Trimethyl-2-pentene	113
Methylcyclopentane	91	*o*-Xylene	120
2,2-Dimethylbutane	92	Ethylbenzene	124
2,3-Dimethylbutane	92	2,4,4-Trimethyl-1-pentene	125
4-Methyl-2-pentene	99	*m*-Xylene	145
Benzene	106	*p*-Xylene	146
C_7 compounds		***C_9 compounds***	
n-Heptane	0	Propylbenzene	127
2-Methylhexane	44	Isopropylbenzene	132
1-Heptene	60	1,3,5-Trimethylbenzene	171

Figure 20: Gasoline components and their RON [19].

2.3.1 Fuel refinement

Crude oil has to be processed in a refinery in order to produce gasoline. The first step is a distillation, the process begins with separations of hydrocarbons, each hydrocarbon has different boiling characteristics, so they become separated into the groups of different molecule sizes. The subsequent process is called cracking, where larger hydrocarbons become broken into the smaller molecules. Then, during reforming, the molecular structure of hydrocarbons can be changed, for example, paraffins can be transformed into the higher-octane aromatics. Finally, unwanted elements such as sulfur can be removed from hydrocarbons in the refining process.

2.3.2 Fuel properties and standards

Spark-ignition engines are powered by gasoline that has to meet European EN228 standards in order to become authorized for sale. Standard EN228 describes the requirements for unleaded gasoline, dedicated to SI-engines. Subsequently, each country has its own additional characteristic values of standards that are attached in the national appendices to general standard EN228. Table 3 presents boundaries of fuel properties specified in EN228 standard [17]. Additionally, there is a comparison of gasoline products from different fuel products in Finland.

Property	Unit	EN228		Fuel			
		Min.	Max.	NESTE Futura 1.1.2017		ST1 and ABC	
				95E10	98E5	95E10	98E5
Octane number	*RON*	95.0	-	96.0	98.7	95.2	98.5
	MON	85.0	-	85.2	87.4	85.7	87.7
Lead content	mg/l	-	5	<2	<2	0	0
Density at 15°C	kg/m^3	720.0	775.0	750	752	750	745
Sulphur content	mg/kg	-	10	7	7	3	5
Oxidation stability	min	360	-	600	500	600	600
Existent gum content	$mg/100ml$	-	5	1	1	1	1
Copper strip corrosion	*rating*	-	1	1	1	1	1
Evaporated at 70°C (E70) - summer	% V/V	22.0	50.0	42.0	32.0	49.0	46.0
Vapour pressure (summer)	kPa	45.0	70.0	67.0	67.0	69.0	69.0
Vapour pressure (winter)	kPa	60.0	90.0	88.0	88.0	88.0	89.0
Vapour lock index	-	-	1250	1094	1011	1135	1250
Evaporated at 70°C (E70) - winter	% V/V	24.0	52.0	44	35	51	48
Evaporated at 100°C (E100)	% V/V	46.0	72	55	51	57	53
Evaporated at 150°C (E150)	% V/V	75.0	-	88	88	88	88
Final boiling point	°C	-	210	187	188	185	188
Olefin content	% V/V	-	18.0	11	11	5	5
Benzene content	% V/V	-	1.0	0.7	0.6	0.8	0.7
Oxygen content	% m/m	-	3.7	3.6	2.6	3.6	2.6
Ethanol content	% V/V	-	10	-	-	9	4.5
Ethers min. 5 carbon atoms	% V/V	-	22	-	-	1	5.5
Aromatic content	% V/V	-	35	31	33	32	33

Table 3: EN228 standard and comparison of gasoline from Finnish fuel producers.

Knocking resistance

Knocking resistance should be maintain at minimum of RON=95 and MON=85 according to EN228 from July 2008 [17].

Ignition temperature

Combustion process has to proceed above the specified minimum temperature where heat is generated by combustion faster than it is lost to the surroundings [24]. This temperature is so-called ignition temperature and from that point combustion becomes self-propagating. Bellow that temperature air-fuel mixture will not burn freely and continuously unless heat is supplied [24]. Both, ignition temperature and flammability limits of air-fuel mixture indicate the ignition potential - Table 4.

Flammability limits

Flammability represents the tendency of a fuel to burn or ignite in the air at specific range of volume concentration. There are two limits of flammability, the lower limit (LFL), which indicates the lower boundary of fuel concentration in the air for spontaneous reaction and upper limit (UFL) which sets highest possible concentration.

Substance	Molecular Formula	Lower Flammability Limit, %	Upper Flammability Limit, %	Ignition Temperature, $^{\circ}C$	References
Carbon	C	—	—	660	Hartman (1958)
Carbon monoxide	CO	12,50	74	609	Scott et al. (1948)
Hydrogen	H_2	4,00	75	520	Zabetakis (1956)
Methane	CH_4	5,00	15	705	Gas Engineers Handbook (1965)
Ethane	C_2H_6	3,00	12,5	520 to 630	Trinks (1947)
Propane	C_3HS	2,10	10,1	466	NFPA(1962)
n-Butane	C_4H_10	1,86	8,41	405	NFPA(1962)
Ethylene	C_2H_4	2,75	28,6	490	Scott et al. (1948)
Propylene	C_3H_6	2,00	11,1	458	Scott et al. (1948)
Acetylene	C_2H_2	2,50	81	406 to 440	Trinks (1947)
Sulfur	S	—	—	190	Hartman (1958)
Hydrogen sulfide	H_2S	4,30	45,5	292	Scott et al. (1948)

Table 4: Ignition temperatures and flammability limits for common fuels [24].

Pressure and temperature influence on flammability, when temperature grows LFL decreases and UFL increases when temperature decreases the effect is reversed for both LFL and UFL. In a case of decreased pressure, LFL increases and UFL decreases, when pressure increases, LFL stays more-less equal, where UFL increases. Important is also the fact that concentration of oxidizer influences flammability limits.

Heating value (caloric value)

Heating value or caloric value is related to the thermal energy in a form of a heat released during the combustion process. This characterizes the energy content of a fuel. There are two types, higher heating value (HHV) and lower heating value (LHV). HHV represents heat produced by complete combustion of a fuel when all products of the process are cooled down to the temperature equal to that before the combustion, and the water vapor formed during combustion is condensed. Whereas, lower heating value, is calculated by subtracting the latent heat of vaporization of the water vapor formed by the combustion from the HHV.

Volatility

Volatility is one of the essential properties of a fuel, it indicates boiling characteristics of the fuel. The volatility of fuels should be kept between minimal and maximal limits. Where, on the one hand, appropriate containment of highly volatile ingredients secures good cold start. But, on the other hand, when volatility is too high, fuel changes its phase from liquid to gas. It causes operational problems of the fuel pump, which leads further to pressure losses in a fuel injection systems. Consequently, it generates problems with starting and decreases performance, especially in the high-temperature environment. This phenomenon is called "vapor lock" and as mentioned before the temperature of environment plays an essential role to adjust correct limitations of volatility. Taking this into account, EN228 set 10 different classes by various levels of a boiling curve, vapor pressure and VLI (Vapor-Lock Index) [11]. Where those values are different for summer and winter. Additionally,

countries can include their own individual classes, that are better suited to their specific climate. In EN228 there are distinguished three temperature values $70^{\circ}C$, $100^{\circ}C$ and $150^{\circ}C$ at which exist both minimal and maximal volume fraction of the fuel that should evaporate. The purpose behind is to ensure that engine will start easily when cold, operate properly when warming-up and evaporates enough much in $150^{\circ}C$ to secure an engine from leaks of non-volatile gasoline components through the cylinder walls into the engine's lubricating oil.

Vapor pressure

Another important fuel's parameter which has specified minimal and maximal boundaries is a vapor pressure (VP). In this case, the compartment between the boundaries ensures that the fuel can be pumped into and out of the vehicle's tank safely. Vapor pressure is measured at $37.8°C$ [11], however, it is good to know VP at higher temperatures (around $80-100°C$) as well. The reason behind is related to the vapor-bubbles formation in the fuel injection systems. This occurs when vapor pressure exceeds system pressure of injectors, which appears especially in fuels that contain a high concentration of alcohols. Vapor/liquid ratio is specifying tendency of given fuel to form bubbles when the temperature rises the vapor/liquid ratio increases as well. Generally, V/L ratio shouldn't exceed 20 volumes of vapor in equilibrium with one volume of liquid in high temperatures (the higher the temperature, the better anti vapor-lock characteristics). Vapor-Lock Index (VLI) describes better the properties of fuel in terms of vapor-lock, hot-starting and hot-running performance than vapor pressure and boiling values alone. VLI is calculated as presented in an equation 2.3.1, and the normal range is between 800 and 1250 [18]. In this case, the lower values, the better anti vapor-lock properties of a fuel.

$$VLI = 10(VP) + 7(E70) \tag{2.3.1}$$

Density

Density is a mass of a fuel per volume at the selected temperature and it is strictly connected with a volumetric energy content of the fuel. The dense the fuel is the greater volumetric energy content it has. Density is a parameter that influences spray formation and mixing characteristics, and at $15°C$ should be between 720 and 775 kg/m^3 [17]. However, premium fuels have a higher density than standard gasoline, because they contain more aromatic compounds. Often there is also used a parameter called **relative density** or **specific gravity**, which is the ratio of the mass of an equal volume of fuel at a specified temperature to the mass of an equal volume of water at the same conditions [25]. Usually, specific gravity for automotive fuels is between 0.70 and 0.78 at $15.6°C$.

Viscosity

Viscosity reflects the resistance of the fluid from deformations by shear stresses or tensile stresses. In other words, the viscosity is a form of "internal friction" of a fluid,

in that sense water has a lower viscosity than honey. Fuels should have specified minimal and maximal boundaries of viscosity, because, this property influences on injection systems and engine performance. When fuel's viscosity is too low, injection spray is too soft, which result in poor mixing and thus power losses. Moreover, it could result in different leakages and power losses. In a case of too high viscosity, sizes of droplets are too big and they last longer in the combustion chamber. This causes poor combustion, increased fuel consumption and higher emissions of HC.

Lubricity

Fuels for internal combustion engines should have good lubricating properties in order to reduce frictions between the surfaces in different parts of the engine [26]. Gasoline should provide good lubrication itself and reduce the wear of engine parts, especially if it comes to injection systems. Some polar substances such as sulfur, act as lubricants. However nowadays sulfur content in the fuel is strictly limited, which is resulting from SOx emissions control policy. Currently, fuels are enriched with different additives in order to provide good lubricating properties.

Purity

Petrol fuel should be visually clear and bright (standard conditions), free from undissolved water, sediment and suspended matter [25]. Nowadays when a lead is removed from fuel, water containment can contribute to the growth of microbes, which subsequently will lead to a chain of unwanted effects. This can occur during refining, distribution or storage. Thus it is very important to control the water content in all possible stages. Contamination of solid and liquid unforeseen additives can cause limitations of fuel metering orifices, corrosion, fuel line freezing, gel formation, filter plugging and fuel pump wear [25].

Sulfur

Sulfur is removed during refining in conjunction with the formation of sulfur oxides that can be transformed into acids during combustion. This is negative both from engine's point of view and emissions. Sulfuric acids content in the fuel results in rusting and corrosion of engine parts and exhaust system. Moreover, sulfur oxides reduce the performance of exhaust gas catalytic converters [25]. On the other hand, SO_x are very harmful atmospheric pollutants causing "acid rain". Thus, the sulfur content in the fuel has to be controlled, maximal sulfur content, shouldn't exceed 50 mg/kg [17]. Fuels that met this requirement are so-called low-sulfur fuels. However, there are also fuels which do not exceed 10 mg/kg [11], they are known as a "sulfur-free" fuels.

Lead

Lead is a harmful compound for a human health and environment, thus currently in Europe leaded gasoline is prohibited and lead content shouldn't exceed 5 mg/l [17].

Gum content

Presence of air in fuel storages can contribute to the oxidation of a fuel, which results in the formation of peroxides or gums. Gums are soluble in the fuel, so they can pass to the fuel injectors, intake manifolds, valves, stems, guides, and ports. Subsequently, because of their sticky character, they can form deposits there. Another undesired effect caused by peroxides are auto-catalytic reaction with fuel system elastomer and copper commutators in the fuel pumps [25]. This formates more peroxides and accelerates devastation of the fuel system components. Moreover, gums and peroxides reduce the octane rating of the fuel, which increases the probability of knocking combustion. Existent gum content in the fuel is limited to 5mg per 100ml [17]. Gum content is reduced by short storage time and special additives (antioxidants), that prevent oxidation and gum formation. Additionally, some metal de-activators can reduce this effect as well.

Corrosion

Corrosion, in general, is a process leading to the destruction of the material by chemical or electrochemical interactions with the environment. The fuel contains trace components such as elemental sulfur, hydrogen sulfide, mercapants, organic acid and water that are reacting with metals in a fuel distribution and vehicle fuel systems causing corrosion and rust formation. Which result in filter plugging and engine wear issues [25].

Fuel additives

Fuel producers use many additives in order to provide or enhance various properties and ensure better operation of an engine. In order to minimize oxidation and gum content, different oxidation inhibitors such as aromatic amines and hindered phenols are used. Additionally, as mentioned previously, metal de-activators such as chelating agents are very good inhibitors for oxidation and gum formation. Carboxylic acids and carboxylates are corrosion inhibitors, where silver corrosion inhibitors include substituted thiadiazoles. Amines, amides, and amine carboxylates are detergents for carburetors and injectors. They prevent and remove deposits in carburetors and port fuel injectors. Additionally, for further cleaning of injectors, intake manifolds, intake ports and valves, polybutene amines and polyether amines are used as deposit control additives. Emulsion formation is commonly reduced by polyglycol derivatives. Engine stalling and starting problems in cold climates are reduced by anti-icing additives such as surfactants, alcohols, and glycols. They prevent ice formation in the carburetors and fuel systems. Antiknock compounds include lead alkyls and methylcyclopentadienyl manganese tricarbonyl (MMT). Additionally, different markers are used for fuel identification, the most common ones are oil-soluble solids, liquid dyes, and organic fluorescent compounds [25].

2.4 Emissions

2.4.1 Pollution formation

The composition of exhaust gases is dependent on many factors such as lambda value (rich or lean combustion), mixture formation, gasoline composition, engine temperature, injection system and many more. Exhaust gases consist of carbon dioxide with the highest share, carbon monoxide, hydrocarbons, nitrous oxides, particulate matter, volatile organic compounds and gaseous components. Exhaust gas composition is highly dependent on air-fuel ratio, whether it is above or below stoichiometric conditions, Figure 21 presents volumetric dependency of each component on air ratio.

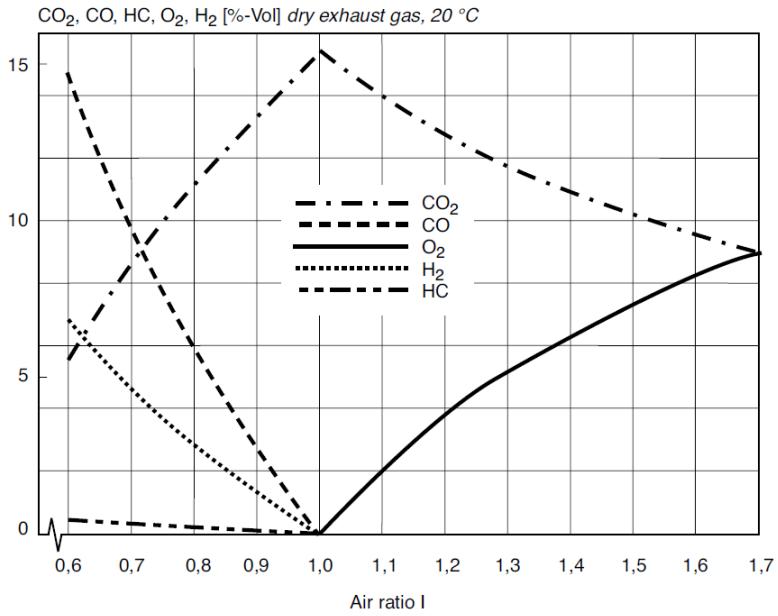


Figure 21: Influance of (λ) on ehxaust gases concentration[21].

Emission of **carbon dioxide** CO_2 comes from the complete combustion of the fuel, whereas **carbon monoxide** CO is a result of intermediate step in the formation of CO_2, and arises from lack of oxygen. Carbon monoxide concentration decreases significantly in an excess air $\lambda > 1$ conditions (figure 21). During incomplete combustion not only CO arises but also unburned or partially **combusted hydrocarbons (HC)**. HC can arise both from fuels and lubricants, incomplete combustion of HC comes from partial ignition of the overall combustion chamber volume, wall deposits and residual fuel in the dead spaces (gaps in the cylinder head seal, valve seats, fire land, piston rings, spark plugs and squish areas) [21]. Moreover, HC emission is highly dependent on combustion chamber's temperature.

Nitrous oxides

Air contains mostly nitrogen (78%), when nitrogen is exposed to high temperatures (combustion chamber) forms nitrogen oxides such as NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4 and N_2O_5, their properties are presented in a table 5.

Formula	Name	Nitrogen Valence	Properties
N_2O	nitrous oxide	1	colorless gas water soluble
NO, N_2O_2	nitric oxide dinitrogen dioxide	2	colorless gas, slightly water soluble
N_2O_3	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO_2, N_2O_4	nitrogen dioxide, dinitrogen tetroxide	4	red-brown gas very water soluble, decomposes in water
N_2O_5	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Table 5: Nitrogen oxides and their properties

There are three main sources of NOx formation, Thermal NO (oxidation of molecular nitrogen in the post-flame zone) described by **extended Zeldovich mechanism**:

$$O + N_2 \rightleftharpoons NO + N \tag{2.4.1}$$

$$N + O_2 \rightleftharpoons NO + O \tag{2.4.2}$$

$$N + OH \rightleftharpoons NO + H \tag{2.4.3}$$

and prompt NO - **Fenimore mechanism** (formation of NO in flame zone), and Fuel-bound NO (oxidation of nitrogen-containing compounds in fuel) [30]. The most hazardous are NO and NO_2, they contribute to acid rain formation, photochemical smog and ground-level ozone. Formation of NO is dependent on temperature, oxygen concentration, air/fuel ratio, dwell time and pressure [21]. Maximal formation of NO occurs at around $1980°C$ to $2280°C$ (rapidly decreases above upper limit) and slightly lean combustion $\lambda = 1.05 - 1.1$ [21]. Spark-ignition engines with direct injection and charge stratification are producing less NO_x emissions (lower average temperature), than SI engines with port injection [21].

Sulfur dioxide

The concentration of SO_x in exhaust gases is proportional to the concentration of sulfur in the fuel. Nowadays, sulfur content is strictly limited in EN228 [17], and it can be considered as a trace emission.

Particulate matter

Particles consist of solid organic or liquid and soluble organic phases, in a form of soot, various sulfates, ash, corrosion products, additives from the fuel and lubricating oil [21]. This kind of emission is not a big issue regarding port-injection SI engines, it is more significant if it comes to diesel engines. However, opposite situation can

be observed for gasoline engines equipped with direct injection system, where PM emissions are significantly higher.

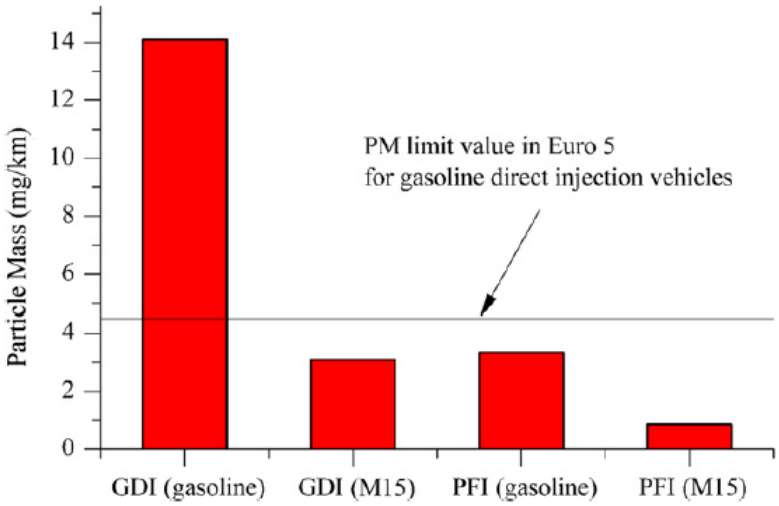


Figure 22: Emission of PM for gasoline direct injection (GDI) engine and port fuel injection (PFI) engine, for two fuels; gasoline and M15 [32].

Figure 22 is comparing emissions of PM for GDI engine and PFI engine fueled by gasoline and M15. PM emission in a case of GDI is significantly higher around 14mg/km, whereas for PFI are slightly over 3. Very interesting is the fact that GDI engine powered by M15 represents significantly reduced emissions of PM, reaching values even lower than for PFI engine fueled with gasoline [32]. It is also worth mentioning that studies have proved similar behavior for ethanol. When the share of ethanol is above 30%, there is an essential reduction of PM in about 30-45% [32]. Thus adding alcohols to gasoline can help to solve the problem of GDI systems increased PM emissions. If it comes to PFI systems, this behavior is preserved and PM emission remains almost negligible.

Other gaseous components

Other gaseous components emission include **aromates:** such as benzene, toluene, xylene, polycyclic aromatic hydrocarbons (PACs). Another group are intermediate products of combustion - **aldehydes:** formaldehyde, hexanal, and benzaldehyde, their formation is sensitive to temperature [21].

Exhaust gas composition

Figure 23 presents composition of exhaust gases of spark-ignition engine powered by gasoline in stoichiometric conditions.

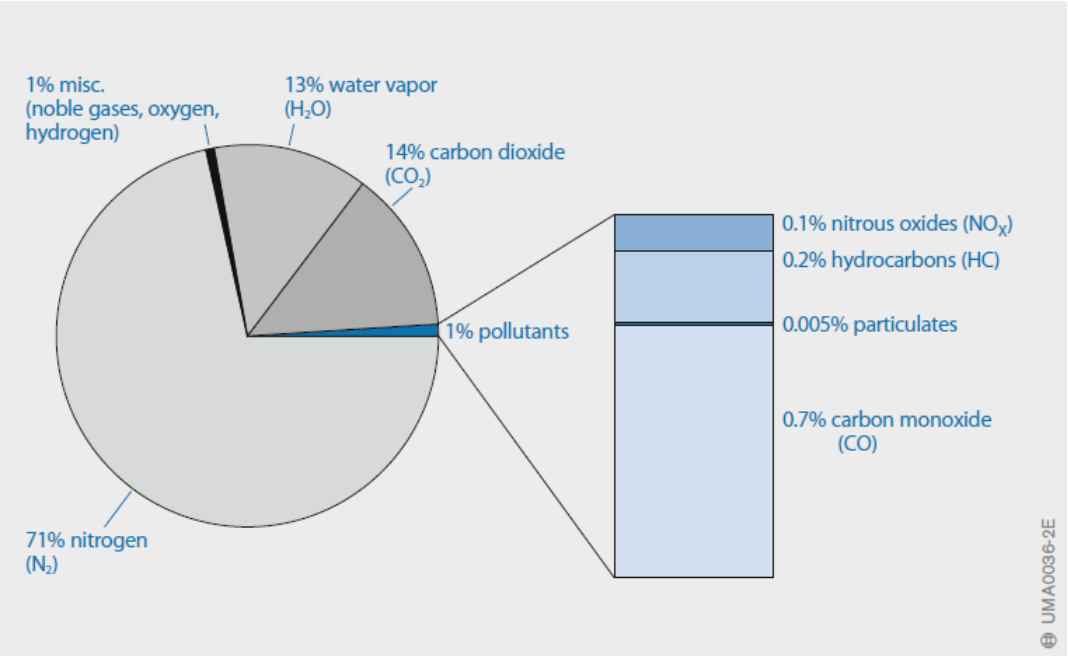


Figure 23: Flue gas composition for SI-engine at $\lambda = 1$ [11].

2.5 Emission control

2.5.1 Three-way catalytic converter

Gasoline engine emission control is carried out by the three-way catalytic converter (TWC) - Figure 24, which is an integral component of the exhaust-emission control system for SI engines [11]. TWC converts hydrocarbons (HC), carbon monoxide (CO), nitrous oxides (NO_x) into water vapor H_2O, carbon dioxide CO_2 and nitrogen N_2 respectively. Converter performs oxidation and reduction processes, CO and hydrocarbons are neutralized in a following way:

Oxidation reaction:

$$2CO + O_2 \rightarrow 2CO_2 \tag{2.5.1}$$

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O \tag{2.5.2}$$

Raction of nitrous oxides reduction:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \tag{2.5.3}$$

$$2NO_2 + 2CO \rightarrow N_2 + 2CO_2 + O_2 \tag{2.5.4}$$

Oxygen needed for those reactions is taken from the exhaust gas or from the nitrous oxides [11]. TWC is very sensitive to air/fuel ratio which should be kept at $\lambda = 1$ in order to assure an appropriate balance of oxidation and reduction reactions.

The catalytic converter can accumulate and release oxygen thanks to ceroxide at substrate layer 2.5.1.

$$2Ce_2O_3 + O_2 \leftrightarrow 4CeO_2 \tag{2.5.5}$$

When $\lambda > 1$, hydrocarbons and carbon monoxide are oxidized by oxygen from the exhaust gas, so HC and CO are not able to perform reduction of NO_x, which remains untreated. In a case of $\lambda < 1$ the situation is reverse, HC and CO reduces NO_x, however, due to the lack of oxygen, excess hydrocarbons and carbon monoxide remains untreated.

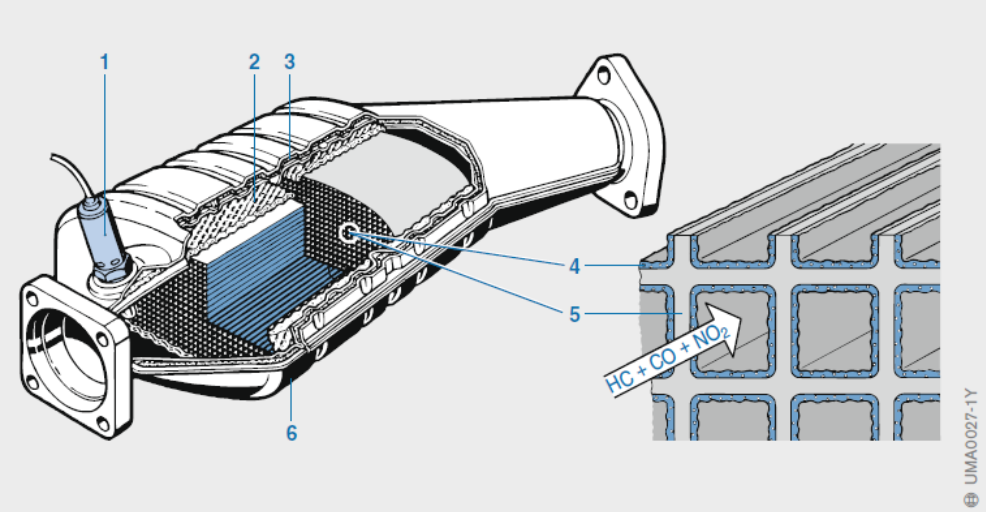


Figure 24: Three-way catalitic converter design [11].

Figure 24 represents the basic design of three-way catalytic converter with the air-fuel (λ) sensor (1). Number 2 is a fastened inside the sheet-steel housing - mineral swell matting which fixes ceramic monolith (that is highly sensitive to mechanical tension) in position and ensures gas seal [11]. Number 3 is a thermally insulated double shell, 4 - wash-coat (Al_2O_3) with a noble-metal coating, 5-monolith and 6 is a case of TWC converter.

2.5.2 Catalysed Gasoline Particulate Filter cGPF

Particulate emissions are significantly higher for direct injection gasoline engines comparing with port injection, as presented in the section 2.4.1. European emission legislation - euro 6(max 0.005g particles emission per km) is forcing the industry to use more efficient after-treatment technologies, especially if it comes to particles. The effective solution is a cGPF - catalyzed Gasoline Particulate Filter, which is very similar to diesel particulate filter (DPF) if it comes to working principle. However, comparing with DPF, particle sizes distribution in gasoline exhaust is shifted towards smaller ones. Moreover, the maximum operating temperature is higher than in the case of DPF, which helps with easier regeneration of the filter[33]. The disadvantage of

this system is resultant pressure drop, which reduces power output and increases fuel consumption. This effect can be reduced by adjusting appropriate GPF dimension and length. GPF can be integrated to TWC, and work simultaneously, reducing CO, HC, NO_x and PM at the same time in one block. There can be applied different design configurations of TWC-GPF system (Figure 25).

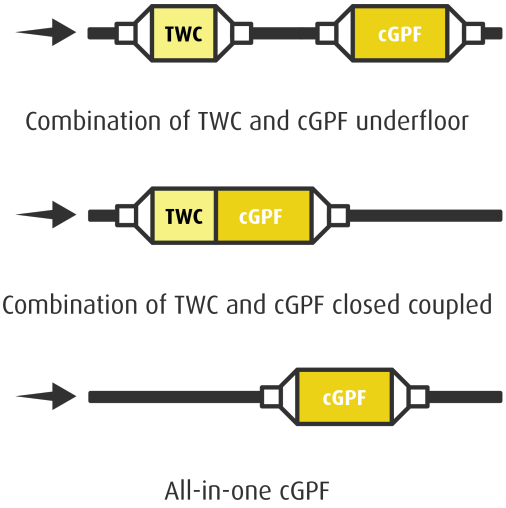


Figure 25: TWC and GPF configurations [33].

3 Methodology

This section presents utilized methodologies and practices in 5 core parts of this project. The first part of this work was extensive literature study, where engine characteristics, combustion process (included related issues), fuel characteristics, emissions and their control methods were studied. Which has covered entire background section. Very important and labor-intensive was data collection part, where over 150 articles were studied. Creation of reliable and universal tools require high-quality input data and thus in the second part data were collected from the most relevant and recent articles, databases, meetings with fuel producers (ST1, NESTE) and OEMs (AVL and VOLVO). During the meetings with industry approach, modeling part and final models were discussed in detail. Valuable advice was of special importance and has increased quality of final models. The third part was sacrificed for data analysis, a creation of database and fuel blend properties modeling tool. The important part of that section was a reduction of articles amount for further use and creation of final matrixes for model development stage. Forth part is a core of this work and is aiming at the development of a numerical tool for prediction of fuel properties impact on engines' fuel consumption and CO_2 emission. The section began with input and output parameters identification, selection of modeling and iteration techniques, parameters optimization model validation and further improvements. At

the end of this part fuel blend properties prediction tool was integrated with engine performance impact tool. The last stage contains consultation and finalizing master thesis. Following sub-chapters are describing in detail chosen alternative fuels, their properties and created tool for prediction of blend properties. Afterward, two most significant approaches: steady-state approach and test cycle procedures are described. The description includes well-defined limitations of each approach method. The last part of methodology chapter presents chosen mathematical modeling and validation procedures.

3.1 Structure of the problem

The essential part is a correct understanding of the problem. Which is of particular importance when considering very complex tasks. In this work, the problem is spat into three parts - fuel properties, engine, and exhaust. The first stage includes identification of the most prominent alternative fuels in accordance with ADVANCE*FUEL* project requirements and selection of the most suitable ones. Subsequently, the most significant properties for fuels and blends need to be indicated. The second part is related to the engine, where it could be recognized that the type of fuel or blend affects fuel consumption and engine efficiency. Additionally, different fuels influence in a different way on engine components. Potential upgrades of present-day technologies include proposed modifications of the engine to make it more suitable for specified alternative fuels. The last part includes exhaust emissions and here only carbon dioxide emissions are taken into account. In that sense, fuel properties affect combustion characteristics and thus influence on carbon dioxide emissions rate.

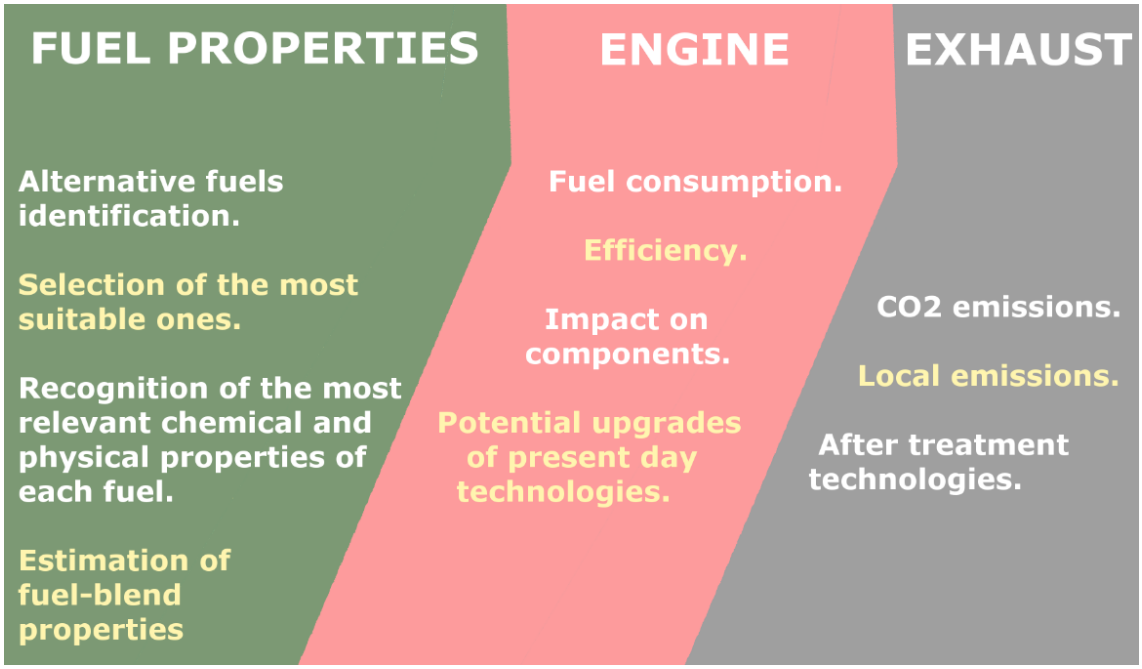


Figure 26: Structure of the problem.

3.2 General approach

Engines for transportation sector could be classified according to their application. This division contains light-duty (passenger cars, vans etc..) vehicles, heavy-duty vehicles, off-road machines, and vehicles. Moreover, there are engines dedicated strictly to specified sectors such as aviation or marine. This division may result in completely different characteristics of engines, especially when comparing land and water transportation engines with aviation sector which uses most commonly jet engines. However, even reciprocating engines vary between each other to such an extent that they require completely different models. Hence, the type of engine needs to be specified in the beginning as an input parameter. Afterward, a set of fuel properties will be introduced into models. This stage could be executed automatically using fuel blend properties calculator, where given fuels and their concentrations in the blend are selected. Subsequently, final values of properties will be calculated and introduced into the models, which in turn will compute fuel consumption and carbon dioxide emissions.

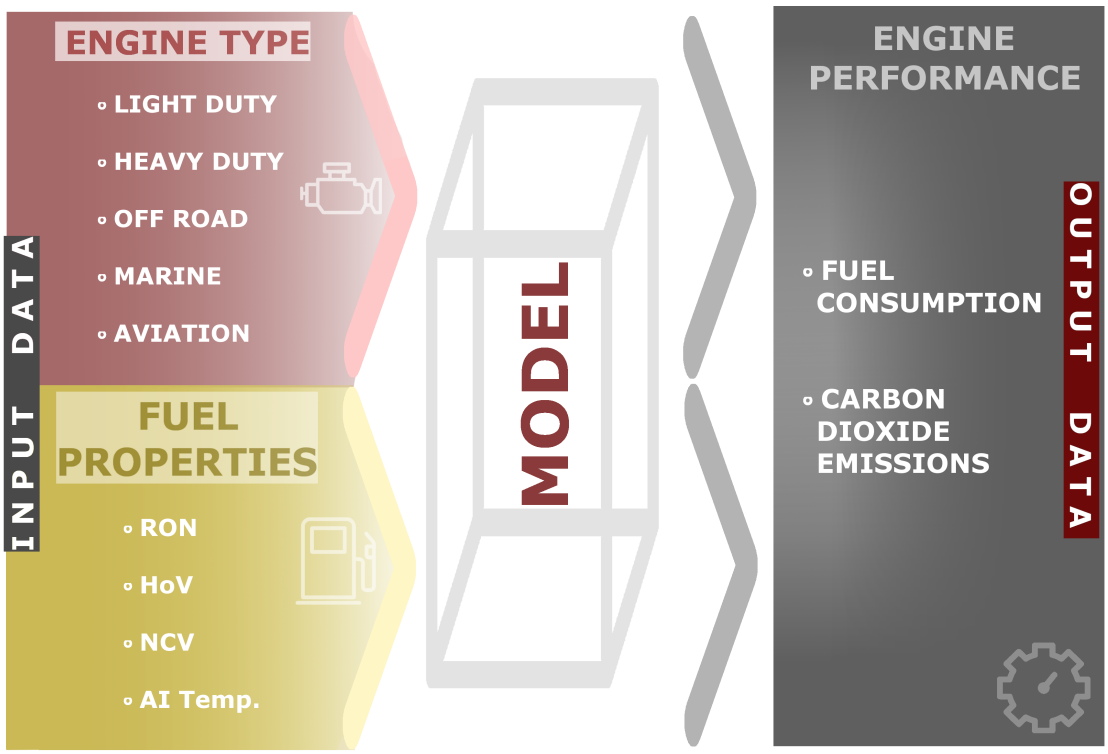


Figure 27: Approach to the problem.

3.3 Gasoline vs alternative fuels for SI engines

Fuels for transportation sector consist of highly sophisticated mixes of different petrochemical compounds. Where standard fuel for spark-ignition engines is a gasoline. However, there are different alternatives such as alcohols or ethers that can

also be utilized in SI engines. If it comes to alcohols, the most relevant are methanol, ethanol, propanol, and butanol. From ethers the most important are MTBE - Methyl Tert-Butyl Ether, ETBE - Ethyl Tert-Butyl Ether, TAME - Tert-Amyl Methyl Ether, TAEE - Tert-Amyl Ethyl Ether, DIPE - Di-Iso-Propyl-Ether. The appendix A, represents values of the most important properties of fuels from alcohol and ether groups. In general, properties of alternative fuels differ from gasoline. Some of them deviate towards desired directions such as octane number, whereas other like calorific value, in general, is lower. In the following subsections, alternative fuels are compared to standard gasoline with particular attention to challenges and benefits connected to each one.

3.3.1 Methanol

Methanol CH_3OH is a colorless liquid which belongs to alcohol group and contains only one atom of carbon. Because of that, methanol combustion is characterized by the lowest emissions of CO_2 compared to other alcohols. Methanol could be successfully produced from renewable feedstock such as wood waste, grass, algae and black liquor [59]. The potential application of this alcohol was found not only in SI but also in CI engines. Challenging part of the fuel is its toxicity, which makes it necessary to use dedicated storages, tanks, refueling systems and several modifications of the engine. If it comes to properties, methanol has higher octane number, both RON and MON are bigger compared to gasoline. Density and heat of vaporization are also higher in the case of methanol. What follows, the net vapor pressure of methanol is roughly a half of gasoline. Characteristic is oxygen content, that reaches half of the total mass of fuel. Methanol has a significantly lower boiling point (Figure A1) compared to gasoline. Freezing point for methanol is $-97,6°C$, which is much lower than for petrol ($-40°C$). Net calorific value of methanol is slightly lower than half of gasoline's, which means that over two times more fuel (methanol) would be utilized in the engine in order to maintain even torque like in the case when running on gasoline.

3.3.2 Ethanol

Ethanol C_2H_5OH is an alcohol, which is nowadays commercially blended with gasoline. Where maximal permitted ethanol content specified in EN228 standard is just 10%. From the fuel producers point of view; 95E10 (of ST1 and ABC companies) contain 9% and 98E5 4,5% of ethanol 3. Similarly to methanol, ethanol can be also produced from first, second and third generation biomass, when additionally it predominates over methanol with lack of toxicity. Ethanol among other alcohols is the most compatible with existing engines, and just several modifications are required in order to run it on SI engine. One of the most important modification is related to increased duration of fuel injection, which is straightforward related to 37,2% lower calorific content of ethanol compared to gasoline (volume base). That base change would allow the engine to run on ethanol fuel. However, in order to ensure proper operation of the engine and preserve its lifetime, more modifications would

be required. Amount of necessary upgrades is dependent on the concentration of ethanol in the blend of gasoline, Figure 28 represents the most important ones.

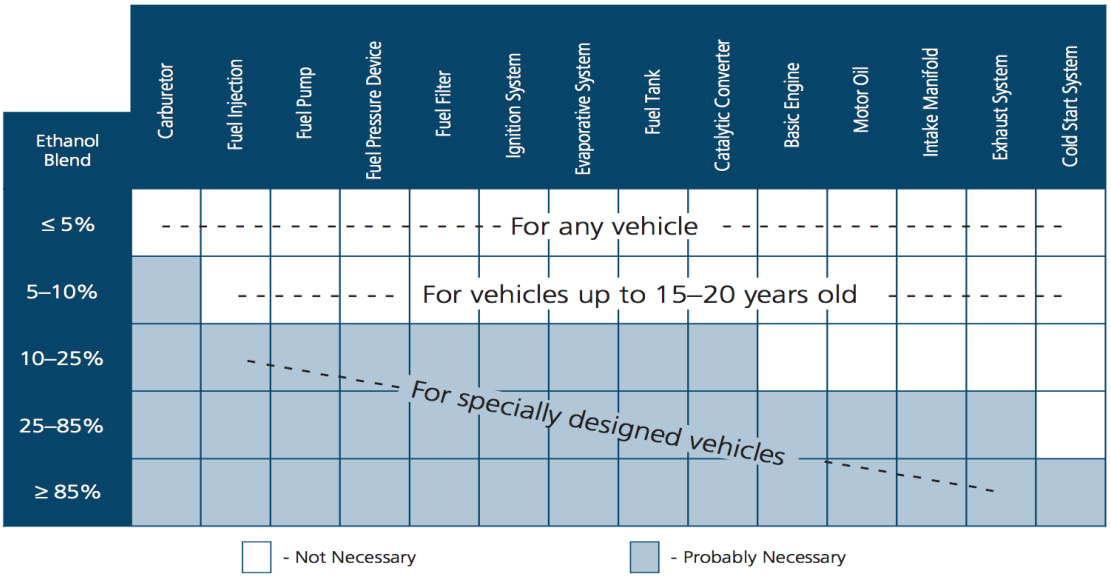


Figure 28: Required adjustments of SI engine for operation with different blends of ethanol and gasoline [60].

Ethanol has 9,44% higher octane number than gasoline, which is very beneficial for fuel producers, especially when talking about utilization of lower quality petrol. Ethanol has around 6% higher density than gasoline, however as mentioned before significantly lower calorific content. Carbon content is 38% lower in ethanol, but oxygen content is over 1200% higher. Ethanol will freeze below $-114°C$ which is very beneficial for cold climate countries.

3.3.3 Propanol

Propanol is a liquid alcohol with colorless appearance, which has three atoms of carbon in the structure. There are two isomers of propanol, isopropanol, and n-propanol. Propanol can be produced from biomass feedstock as aforementioned alcohols. However, it is rarely considered to be used as a fuel, because of high production costs comparing with other alcohols [61]. Propyl alcohol is sometimes called "rubbing alcohol" or "gas dryer" because of it's drying properties. Although n-propanol keeps water in solution with gasoline, it prevents water from freezing in gas lines [61]. From the properties point of view, both isomers represent high octane number (above 108). N-propanol has a higher density than isopropanol, where at the same time both values are bigger than gasoline's density. Propanol (included both isomers) has just around 16% higher calorific value than ethanol, which is still 25% lower than gasoline's NCV (volume base). Additionally, taking into account high production costs of propanol, one can say that ethanol is more feasible

commercially. Freezing temperature for n-propanol is the lowest among alcohols and is equal $-127°C$, where for isopropanol is just $-90°C$.

3.3.4 Butanol

Butanol as all alcohols is in a form of colorless liquid. Butyl alcohol contains four atoms of carbon in the molecular structure. There are four isomers of butanol: isobutanol, n-butanol, 2-butanol, and tetr-butanol. Butanol compared to other alcohols such as propanol ethanol or methanol is the most similar to gasoline from the properties perspective. Which in turn allows butanol to be used in SI engines without major modifications. It concerns full blend concentration spectrum (even pure butanol) [65]. Among isomers of butanol, the highest octane number 103,5 has isobutanol, where the lowest occur in n-butanol. If it comes to density, the highest has n-butanol and the lowest tetr-butanol. Butanol has significantly higher Heat of vaporization, over 520 kJ/kg, and much lower net vapor pressure. Where the lowest value is observed for sec-butanol 1,67 kPa at $37,8°C$ and the highest 12kPa for tetr-butanol (which is still around six times lower than gasoline's NVP). Butanol's net calorific value is around 20% lower compared to gasoline, but it is the highest number of aforementioned alcohols. If it comes to the production of butanol, biomass feedstocks could be utilized (included first and second generation). However, challenging part is related to the traditional fermentation process, where small concentrations of butanol are toxic to microorganisms [65]. The comforting fact is that butanol can be produced in a cost-effective manner from ethanol. Additionally, infrastructure for ethanol production could be successfully upgraded to butanol production with minor investment [65].

3.4 Selected fuels

In order to meet objectives of this project, it is important to use commercially mature and feasible alternative fuels, that are already very well tested and show great potential for replacing fossil fuel (gasoline). **Fuels taken into further considerations are methanol, ethanol and butanol blends with gasoline**. Their final properties, impact on SI engine performance indicators and related emissions were collected for development of the numerical tool. It is worth mentioning that alternative fuels blends were tested as drop-in fuels. Where, in reality, drop-in fuels are fully interchangeable with standard fuels. This, in turn, means that they can be stored in the same tanks, refueled in the same way and they do not require any engine modifications. However, as mentioned in previous chapter 3.3 "Gasoline vs alternative fuels for SI engines", methanol's toxicity and significant difference between properties of other chosen alternative fuels would lead towards engine modifications. This is necessary, especially when talking about higher concentrations in the blend or running engine solely on alternative fuel. Currently, there is so-called "blending wall" which is referring to the amount of alternative fuel (for ex. ethanol) which is allowed to be blended with petroleum-based fuel (gasoline in this case) [58]. Blending wall is a form of a safe compartment, in which specified alternative fuel could be blended as drop-in-fuel.

3.5 Fuel properties selection and prediction tool

Fuel properties (described in background 2.3) affect engine performance indicators. The main task of this project is to obtain models that describe how fuel properties affect fuel consumption and CO_2 emissions. The first step towards this problem is to indicate which properties affect specified components or parameters of combustion and engine in general. Therefore, following division is introduced:

- **Duration of fuel injection:**
  - heating value,
  - density.
- **Ignition characteristics and quality:**
  - octane number (RON, MON),
  - autoignition temperature,
  - flammability limits.
- **Combustion characteristics (included mixture formation):**
  - heat of vaporization,
  - vapor pressure,
  - volotality,
  - density,
  - oxygen content.
- **Operational aspects:**
  - viscosity (fuel supply system),
  - existent gum content (fouling of intake valves),
  - density (fuel supply system),
  - lubricity (engine and components life time),
  - Freezing point (cold start issues).
- **Exhaust emissions and fouling:**
  - aromatics content,
  - sulfur content,
  - carbon residue,
  - lead content,
  - existent gum content,
  - ash,
  - total contaminants.

- **Safety, storage and refueling:**
  - flash point,
  - corrosiveness,
  - toxicity,
  - oxidation stability,
  - compatibility with materials.

3.5.1 Selected fuel properties

The second step is connected to the extraction of properties that affect fuel consumption the most. Thus, first three groups featured above are considered as especially important ones. Selection of fuel properties that affect the most is a crucial part for further considerations. In the modeling part, it is important to avoid introduction of strongly interrelated parameters, especially when talking about linear fitting. Thus net calorific value mass based (NCVmass) and density were replaced by net calorific value volume based (NCVvol). The oxygen content is strongly interrelated with other properties such as NCV. Thus, it was decided to omit it as an input parameter. Flammability limits haven't been considered in the model. However, autoignition temperate and octane number were taken into account. Vapor pressure, the heat of vaporization and volatility are interrelated parameters, and thus heat of vaporization was chosen as an input parameter. Summarizing, following 4 parameters were selected for modeling part:

- Octane number (ON),
- Heat of Vaporization (HoV),
- Net Calorific Value volume based (NCVvol),
- Auto Ignition Temperature (AIT).

3.5.2 Fuel Blend Property Calculator

In order to create the tool that predicts fuel blend properties impact on SI engine's fuel consumption and emissions, it is needed to predict fuels blend final properties that are listed above. This tool is especially valuable when talking about fuel properties of unconventional blends. As mentioned in the chapter *Selected fuels* 3.4, only alcohols were taken into account during modeling part. However, final models are not limited only to alcohols. Input parameters are numbers from 1 to 4 and concentration from 0 to 100%. The number is related to the amount of carbon atoms in the molecule of alcohol, where 1 is methanol, 2-ethanol, 3-isopropanol, and 4-isobutanol. Concentration is related to the blend of gasoline, where 0% means pure gasoline and 100% corresponds to the full concentration of chosen alcohol. After introducing input data, fuel blend property calculator (FBPC) computes final values of the blend

parameters based on adjusted linear and non-linear models. Structure of the tool is presented in the Figure 29.

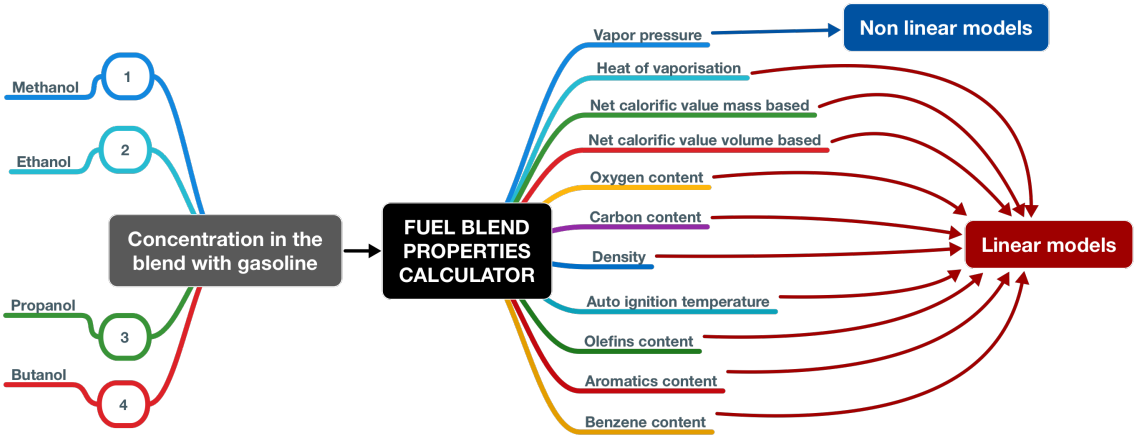


Figure 29: Working structure of the fuel blend properties calculator.

Among all properties, vapor pressure manifests in non-linear behavior, and thus polynomial function was fitted. Values of ethanol, isopropanol and isobutanol VP for modeling were obtained from following article B.M. Masum*, H.H. Masjuki, M.A. Kalam*, S.M. Palash, M. Habibullah *"Effect of alcohol-gasoline blends optimization on fuel properties, performance and emissions of an SI engine"* [66]. Methanol VP values were examined in V. F. Andersen,† J. E. Anderson,*,‡ T. J. Wallington,*,‡ S. A. Mueller,‡ and O. J. Nielsen† "Vapor Pressures of Alcohol-Gasoline Blends" [67]. Extracted values are presented in the Table 6

	Concentration [%]	Vapor Pressure at 37.8 $^{\circ}C$ [kPa]			
		Methanol	Ethanol	Isopropanol	Isobutanol
Gasoline	0	60,00	60,00	60,00	60,00
	10	84,66	68,73	63,38	58,26
	20	84,00	67,28	61,09	55,38
	30	82,82	65,24	58,81	52,47
	40	80,73	62,59	55,67	48,51
	50	78,64	59,07	51,84	44,74
	60	74,34	53,89	46,90	37,78
	70	70,04	47,59	41,00	31,22
	85	56,40	34,37	28,55	17,92
Alcohol	100	31,30	15,15	11,38	1,57

Table 6: Vapor pressure for alcohol-gasoline blends at 37.8$^{\circ}C$ [66], [67].

Subsequently, 6th power polynomial functions were fitted. In the Figure 30 continuous lines represent adjusted functions for each alcohol-gasoline blends.

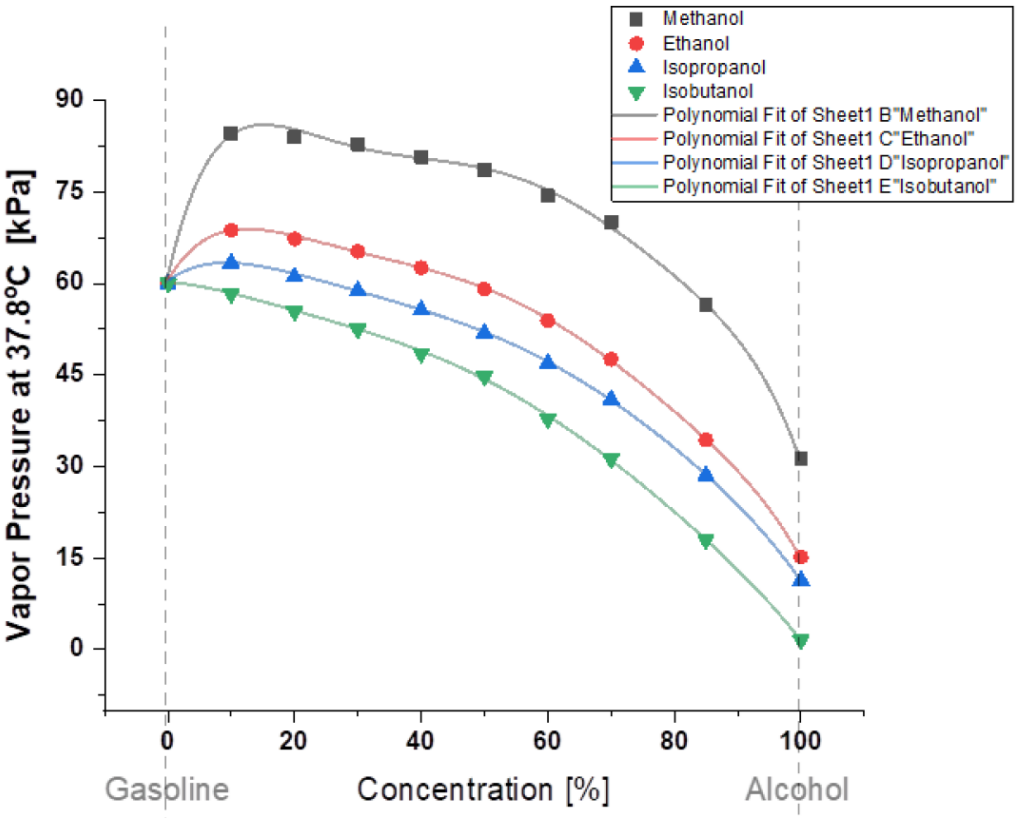


Figure 30: Modeling of vapor pressure for alcohol-gasoline blends at 37.8°C.

As presented above, high accuracy was obtained R-square and adjusted R-square values are over 0.99. The body of matched polynomial functions, values and errors of parameters are presented in the Figure 31.

Equation	y = Intercept + B1·x^1 + B2·x^2 + B3·x^3 + B4·x^4 + B5·x^5 + B6·x^6			
Plot	Methanol	Ethanol	Isopropanol	Isobutanol
Weight	No Weighting			
Intercept	60,12368 ± 1,12037	60,04221 ± 0,37428	60,03703 ± 0,32122	60,00381 ± 0,47343
B1	4,68899 ± 0,44718	1,79725 ± 0,14939	0,79771 ± 0,12821	-0,04902 ± 0,18896
B2	-0,31111 ± 0,04878	-0,12938 ± 0,0163	-0,06519 ± 0,01399	-0,01861 ± 0,02061
B3	0,00951 ± 0,00204	0,00404 ± 6,82972E-4	0,00198 ± 5,86156E-4	7,21999E-4 ± 8,63893E-4
B4	-1,49045E-4 ± 3,95626E-5	-6,54688E-5 ± 1,32165E-5	-3,15443E-5 ± 1,1343E-5	-1,44638E-5 ± 1,67176E-5
B5	1,1509E-6 ± 3,56247E-7	5,1583E-7 ± 1,1901E-7	2,4323E-7 ± 1,0214E-7	1,27734E-7 ± 1,50536E-7
B6	-3,49905E-9 ± 1,20703E-9	-1,58578E-9 ± 4,0323E-10	-7,35229E-10 ± 3,46069E-10	-4,20392E-10 ± 5,10046E-10
Residual Sum of Squares	3,78298	0,42218	0,31097	0,67548
R-Square (COD)	0,99853	0,99984	0,99988	0,99979
Adj. R-Square	0,99558	0,99951	0,99963	0,99938

Figure 31: Modeling parameters of vapor pressure for alcohol-gasoline blends at 37.8°C.

Remaining parameters were modeled by linear functions. The heat of vaporization increases linearly with the growth of alcohols in the blend of gasoline [68], [69]. Net Calorific Values both mass and volume based are clearly decreasing linearly with the growth of alcohol concentration. However, octane number increases when gasoline content decreases in the blends with alcohols. Those behaviors are presented in the Figure 32, where additionally linear fitting was performed.

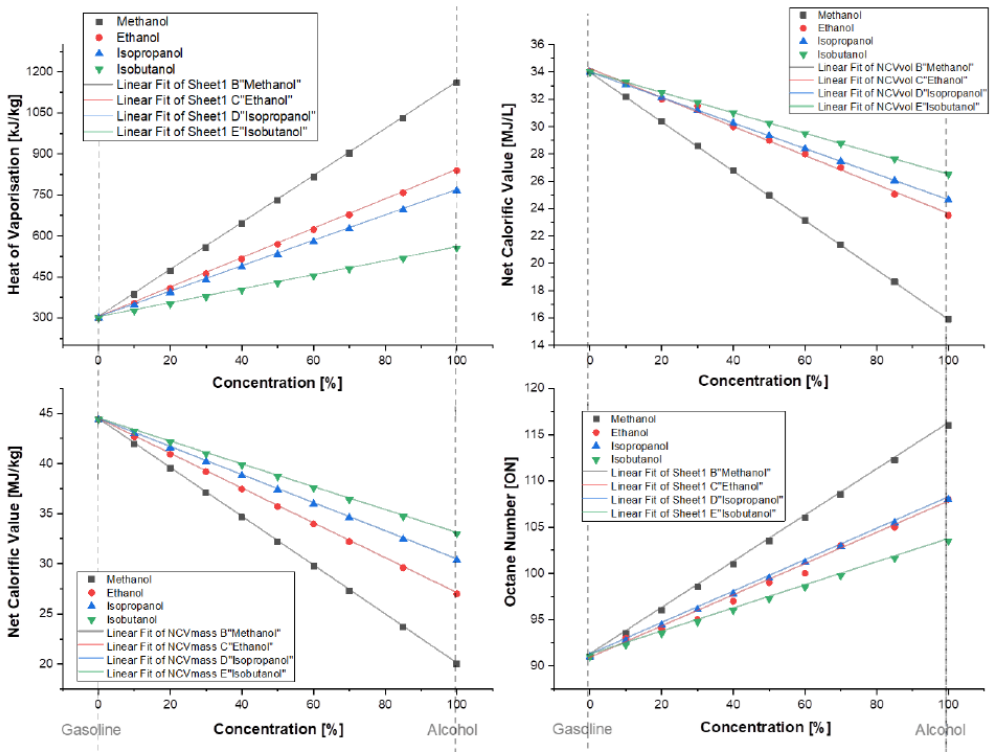


Figure 32: Dependence of HoV, NCVmass, NCVvol and ON on increasing concentration of alcohols in the blend with gasoline.

Modeling parameters, accuracy and related errors are listed in the Figure 33.

Equation	y = a + b·x			
Plot	**Methanol**	**Ethanol**	**Isopropanol**	**Isobutanol**
Heat of vaporisation				
Intercept	300 ± 7,53681E-14	300 ± 3,0456E-14	300 ± 1,83454E-14	300 ± 3,97253E-14
Slope	8,6 ± 1,34876E-15	5,39 ± 5,45032E-16	4,655 ± 3,28303E-16	2,56 ± 7,10913E-16
R-Square (COD)	1,00E+00	1,00E+00	1,00E+00	1,00E+00
Adj. R-Square	1	1	1	1
Net calorific value (volume based)				
Intercept	34 ± 0	34,25875 ± 0,12202	34 ± 4,91847E-15	34 ± 0
Slope	-0,1808 ± 0	-0,10614 ± 0,00218	-0,0935 ± 8,80196E-17	-0,075 ± 0
R-Square (COD)	1	0,99663	1	1
Adj. R-Square	1	0,9962	1	1
Net calorific value (mass based)				
Intercept	44,4 ± 4,95273E-15	44,4 ± 4,3578E-15	44,4 ± 1,47662E-15	44,4 ± 1,32875E-15
Slope	-0,244 ± 8,86327E-17	-0,174 ± 7,79858E-17	-0,1404 ± 2,64252E-17	-0,114 ± 2,37789E-17
R-Square (COD)	1	1	1	1
Adj. R-Square	1	1	1	1
Octane number				
Intercept	91 ± 0	90,64306 ± 0,30919	91 ± 2,22216E-15	91 ± 0
Slope	0,25 ± 0	0,16897 ± 0,00553	0,17 ± 3,97671E-17	0,125 ± 0
R-Square (COD)	1	0,99149	1	1
Adj. R-Square	1	0,99043	1	1

Figure 33: Modeling data for HoV, NCVmass, NCVvol and ON relation to increasing concentration of alcohols in the blend with gasoline.

The subsequent part of modeling was related to oxygen and carbon content, the density at $15°C$ and autoignition temperature. All parameters are characterized by a

linear relation with the growth of alcohols concentration, where only carbon content decreases and remaining ones increase.

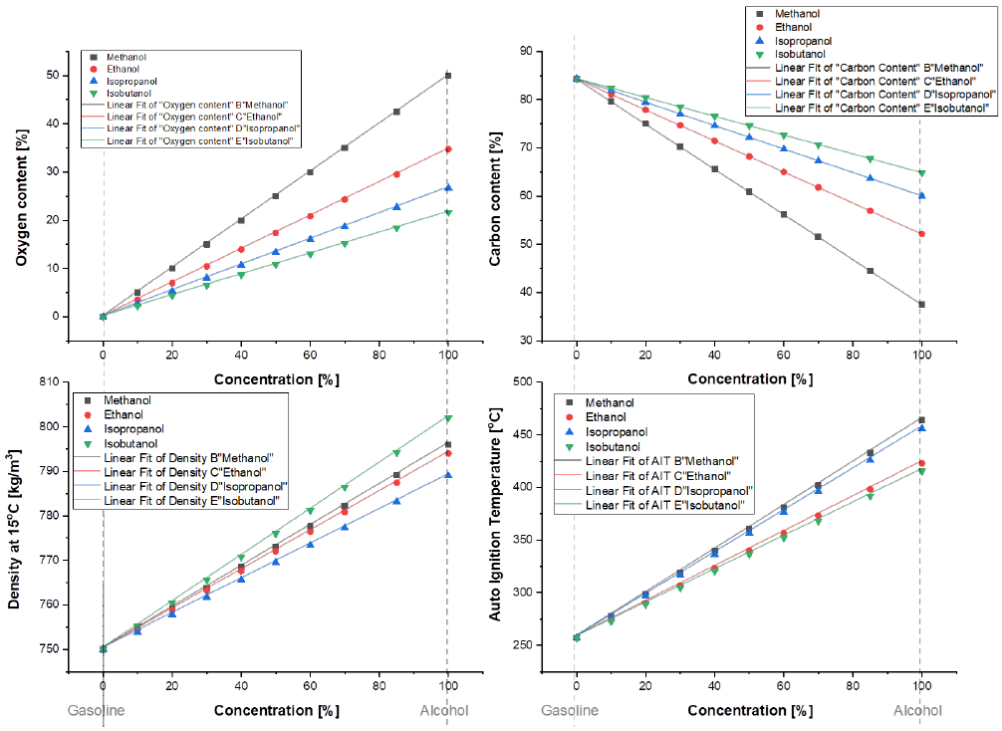


Figure 34: Dependence of oxygen content, carbon content, density and auto ignition temperature on increasing concentration of alcohols in the blend with gasoline.

Modeling parameters, accuracy and related errors are listed in the Figure 35.

Equation	y = a + b·x			
Plot	Methanol	Ethanol	Isopropanol	Isobutanol
Oxygen content				
Intercept	0 ± 0	0 ± 7,16266E-16	77636E-15 ± 1,64117E-	0 ± 0
Slope	0,499 ± 0	0,347 ± 1,28181E-17	0,2667 ± 2,93699E-17	0,2162 ± 0
R-Square (COD)	1	1	1	1
Adj. R-Square	1	1	1	1
Carbon content				
Intercept	84,31 ± 8,13719E-15	84,31 ± 2,58253E-15	84,31 ± 4,09902E-15	84,31 ± 7,38744E-15
Slope	-0,4681 ± 1,45621E-16	-0,3221 ± 4,62163E-17	-0,2431 ± 7,33548E-17	-0,1951 ± 1,32203E-16
R-Square (COD)	1	1	1	1
Adj. R-Square	1	1	1	1
Density				
Intercept	750 ± 7,57764E-14	750 ± 7,31714E-14	750 ± 1,74434E-14	750 ± 1,94384E-14
Slope	0,46 ± 1,35607E-15	0,44 ± 1,30945E-15	0,39 ± 3,12161E-16	0,52 ± 3,47864E-16
R-Square (COD)	1	1	1	1
Adj. R-Square	1	1	1	1
Auto Ignition Temperature				
Intercept	257 ± 1,02554E-14	257 ± 4,20406E-14	257 ± 3,35958E-14	257 ± 1,2813E-14
Slope	2,07 ± 1,83527E-16	1,66 ± 7,52346E-16	1,99 ± 6,01221E-16	1,586 ± 2,29297E-16
R-Square (COD)	1	1	1	1
Adj. R-Square	1	1	1	1

Figure 35: Modeling data for oxygen content, carbon content, density and auto ignition temperature relation to increasing concentration of alcohols in the blend with gasoline.

The last part of FBPC was related to modeling of olefin, aromatics and benzene concentrations in the blends. Alcohols are single chemical compounds, which means that in pure solution there are no olefins, aromatics, and benzene. Thus one function for each component will be suitable to all alcohols taken into consideration. Following Figure 36 represents how the concentration of mentioned above components decreases with the growth of alcohols in the blend with gasoline. Figure 36 includes adjusted linear functions.

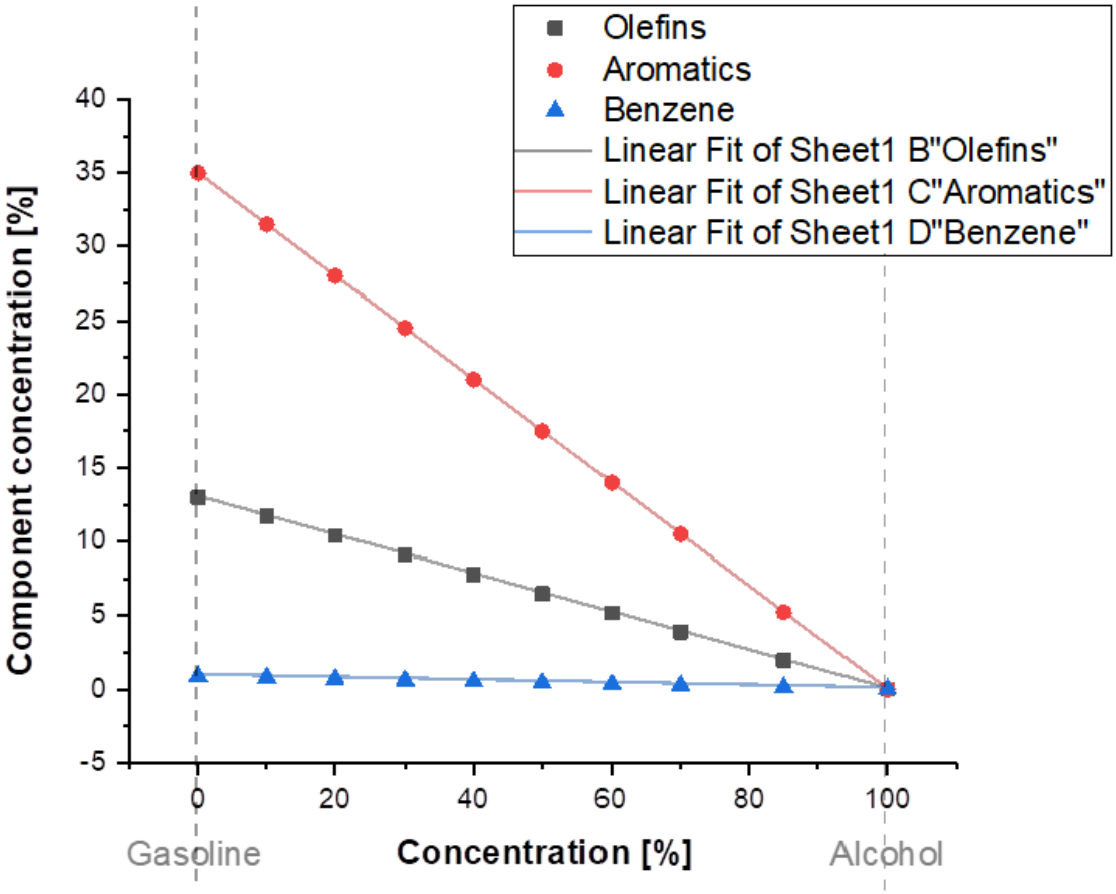


Figure 36: Olefin, aromatics and benzene concentration dependency on alcohol concentration growth in the blend with gasoline.

Modeling parameters, accuracy and related errors are listed in the Figure 37.

Equation	y = a + b·x		
Plot	Olefins	Aromatics	Benzene
Weight		No Weighting	
Intercept	13 ± 9,64302E-16	35 ± 2,82562E-15	0,9 ± 1,04875E-16
Slope	-0,13 ± 1,72569E-17	-0,35 ± 5,05665E-17	-0,009 ± 1,87681E-18
R-Square (COD)	1	1	1
Adj. R-Square	1	1	1

Figure 37: Modeling data for olefin, aromatics and benzene concentration dependency on alcohol concentration growth in the blend with gasoline.

3.6 Detailed approach

Fuel properties affect engine performance and emissions in different ways, determination of how do they impact is a very challenging task. Solving that kind of complex problems require careful selection of appropriate approach. In general there are three possibilities, first one is based on steady-state measurements, second in driving cycles and third on combustion characteristics (physics of processes and chemistry of proceeding reactions) - Figure 38.

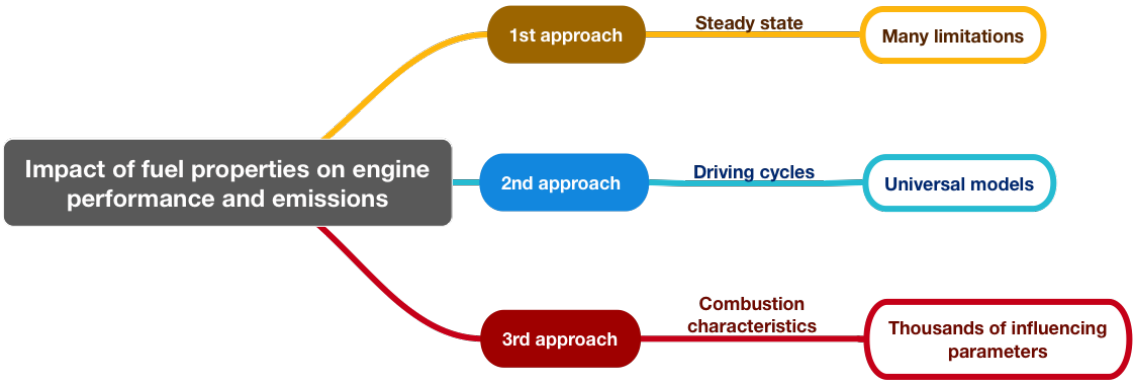


Figure 38: Possible approaches

This work is related mainly to light-duty vehicles, where the steady-state approach is involved with many limitations. The main ones contain the impact of engine operating parameters such as load (Brake Mean Effective Pressure - BMEP) or engine speed (Mean Piston Speed - MPS). Driving cycle based models are in this case more universal and representative. The last approach which hasn't been taken into account in the scope of this project is based on combustion characteristics (physics of processes and chemistry of proceeding reactions). 3rd approach is extremely complex and hard to solve because of thousands influencing parameters.

3.6.1 Steady state approach

Modeling of fuel properties impact on engine performance and emissions based on steady-state approach results in different models for each engine operating point (specified by speed and load). If it comes to SI engine, engine speed is controlled by so-called TPS - Throttle Position Sensor, where engine load in laboratory conditions is controlled by dynamo-meter (Figure 39). Engine speed could be also expressed by mean piston speed and load could be converted into brake mean effective pressure. In the steady state approach engine performance is expressed by BSFC - Brake Specific Fuel Consumption, Brake Power, and BTE - Brake Thermal Efficiency. Emissions in the steady-state approach are expressed as specific emissions (described in 2.1.3). Modeling process requires high quality and reliable data, where additionally commercially available fuels and engines were used. In steady state approach engine's displacement and fuel injection method also matters and affects final results.

Figure 39: Laboratory setup of VOLVO spark ignition engine connected to the dynamometer. Aalto University research group of Thermodynamics and Combustion Technology.

There were chosen four different articles for steady state analysis. First one [70] (from 2011) was measuring compression ratio impact on engine performance using ethanol blends with gasoline. Tests were performed in 4 strokes, 4 cylinders, 8 valves and 1L of displacement spark ignition engine. Three compression ratios 10:1, 11:1 and 12:1 were applied in a steady state conditions (NBR/ISO 1585 standard [74]). Measurements were carried out from 1500rpm to 6500rpm with the increments of 250rpm. Throttle position was at WOT point during all measurements [70]. Tested fuels were E5, E22, and E100.

Second source [71] (2008) was testing the impact of gasoline and ethanol blends affect on performance and emissions. Applied SI engine was 4 stroke, 4 cylinders, 8 valves, 1,323L of displacement and compression ratio 9.7:1, which is slightly lower than the one used in the first source. Measurements were carried out from 1000rpm to 5000rpm with the intervals of 500rpm. Throttle position was fully open (WOT) during all measurements [71]. Tested fuels were: pure gasoline, E5, E10, E15, and E20.

Third article's [72] topic is very similar to the second source. However, test engine is different, have just 1 cylinder and larger displacement 1,795L. Compression

ratios were 10:1 and 11:1. The tests were performed for different engine speeds from 1500rpm to 5000rpm with the intervals each 500rpm. Throttle device was at the fully open position during the measurements. There were examined pure gasoline and ethanol-gasoline blends: E50 and E85.

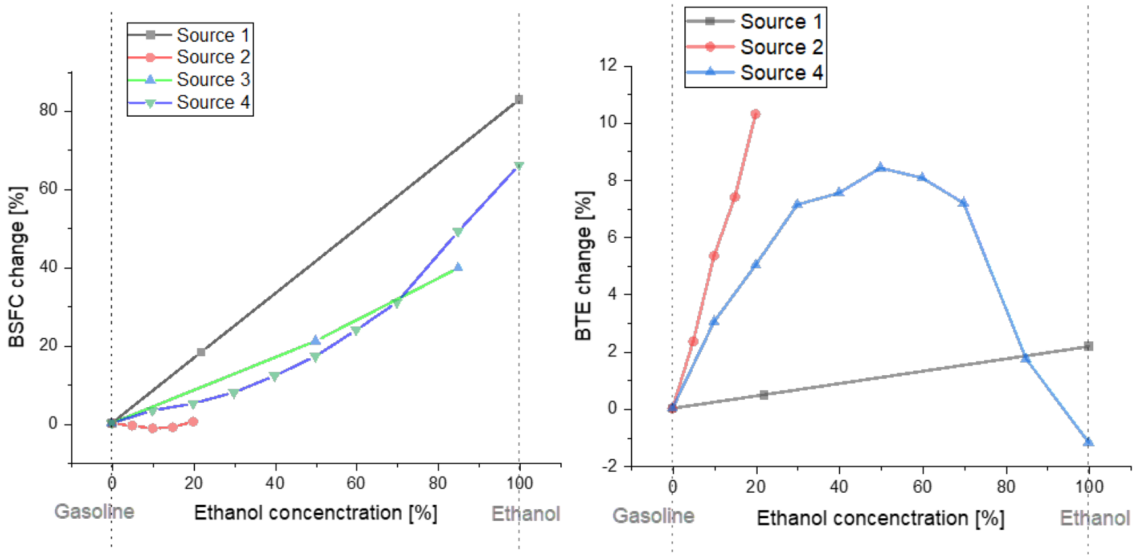
Forth and the most sophisticated source [73] (2016) was studying the optimal blending ratio of ethanol and gasoline to achieve better SI engine performance. The test engine is made by Toyota, model: 3ZZ-FE [75], which is a 4 stroke, 4 cylinders, 16 valves engine with the total displacement of 1,6L and compression ratio 10,5:1. The procedure of measurements was at 4 different throttle positions, 15% WOT, 30% WOT, 45% WOT and 60% WOT. Tests were carried out for 6 chosen engine speeds ranging from 2000rpm to 4500rpm with the 500rpm increments. There were examined ethanol-gasoline blends: E10, E20, E30, E40, E50, E60, E70, E85 and pure ethanol - E100. All data described above are summarized in the Figure 40.

Source	Source	1		2		3	4	
	Year	2011		2009		2009	2016	
	Country	Brasil		Iran		Turkey	Thailand	
Engine operation conditions	Load	Wide Open Throttle (WOT)						
	Speed	3000 RPM						
Engine	Nr. of cylinders	4		4		1	4	
	Nr. Of valves	8		8			16	
	Bore [mm]	70		71		80,26	79	
	Stroke [mm]	64,9		83,6		88,9	81,5	
	Displacement [cm3]	999		1323		1798	1598	
	Compression Ratio	10:1		9.7:1		10:1	10.5:1	
Engine Performance		BSFC	BTE	BSFC	BTE	BSFC	BSFC	BTE
		g/kWh	%	g/kWh	%	g/kWh	g/kWh	%
Fuels	Gasoline	232,86	33,16	252,58	31,88	264,38	269,87	30,23
	E5			250,93	32,63			
	E10			249,28	33,58		278,63	31,15
	E15			249,90	34,24			
	E20			253,61	35,16		283,42	31,75
	E22	275,31	33,31					
	E30						291,10	32,39
	E40						302,60	32,51
	E50					319,98	316,03	32,78
	E60						334,25	32,67
	E70						353,42	32,41
	E85					369,35	402,33	30,76
	E100	425,80	33,87				448,36	29,88

Figure 40: Chosen articles for steady state analysis. Specification of test engines, blends and engine performance outputs. Source 1: [70], source 2: [71], source 3: [72], source 4: [73].

From the data presented above relative to gasoline percentage changes of BSFC and BTE were calculated for all chosen sources. Subsequently, outputs for selected

engine operation conditions: WOT and 3000rpm were plotted (Figure 41a and 41b). If it comes to BSFC, there is a significant difference between the sources, where first one [70] deviates the most from others. Brake thermal efficiency 41b manifests in completely different behavior in each source.



(a) BSFC.

(b) BTE.

Figure 41: Comparizon of BSFC and BTE changes from 4 chosen sources. Source 1: [70], source 2: [71], source 3: [72], source 4: [73].

Besides different results from various sources, there is another significant challenge related to the impact of engine operating conditions. Throttle position and engine speed in steady state approach affect engine performance strongly. Based on the source 4 [73], relative percentage changes of BSFC and BTE were calculated for 2000rpm and 4500rpm at four different throttle positions (15% WOT, 30% WOT, 45% and 60%). The purpose was to examine how exactly engine operational conditions affect results. If it comes to brake specific fuel consumption, maximal change (141,28% growth) at 4500rpm (comparing to 2000rpm) could be observed for E100 fuel at 15% WOT. Whereas the lowest change of BSFC (5,22% growth) is observed for E10 fuel at 60% WOT. However, the highest value of BSFC (1066,22 g/kWh) has E100 fuel at 4500rpm and 15% WOT, whereas minimal BSFC (274,6922g/kWh) is observed for E10 Fuel at 2500rpm and 30% WOT. If it comes to BTE, the highest change (58,58% drop) at 4500rpm (comparing to 2000rpm) is observed for E100 fuel at 15% WOT. Whereas the lowest change of BTE belongs to E20 fuel at 45% WOT. The highest brake thermal efficiency (32,779%) has E50 fuel at 3000rpm and 60% WOT, where the lowest (12,607%) - E100 at 4500rpm and 15% WOT. Figure 42 represents changes of BSFC and BTE for different throttle positions.

Based on the results it could be clearly stated that for the same fuel, BTE and BSFC can take different values depending on the engine speed and throttle position.

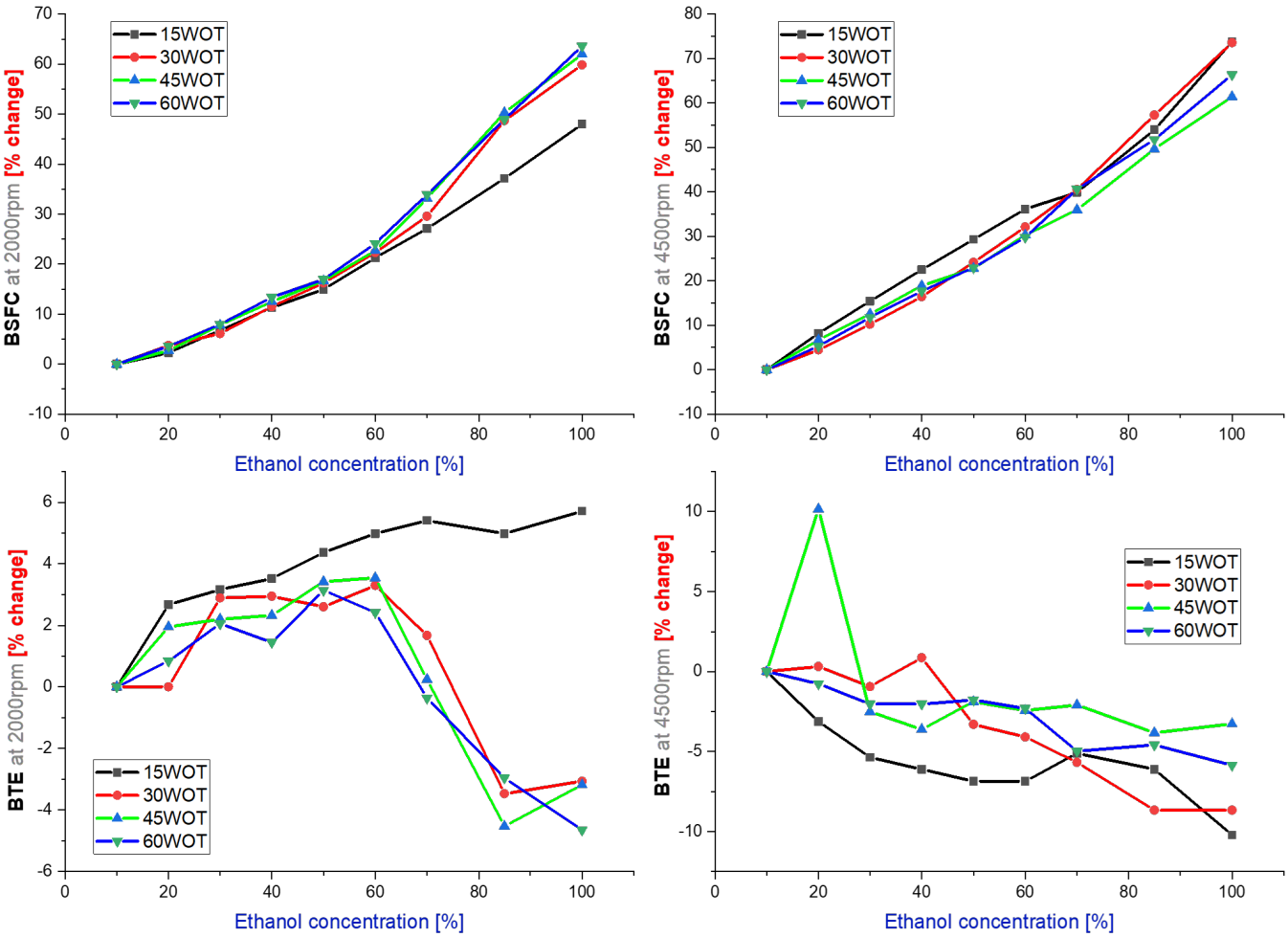


Figure 42: Changes of BSFC and BTE at 2000rpm (left side) and 4500rpm(right side) for four different throttle prositions 15% WOT, 30% WOT, 45% and 60%. Made based on [73].

3.6.2 Driving cycles approach

The second approach is based on the driving cycles that are a compilation of many steady-state points with additionally transient operating conditions. Driving cycles were introduced to measure in a more reliable way average fuel consumption and emissions during real driving conditions. First version of **European Drive Cycle (EDC)** was introduced between 1960s and 1970s [76]. Tests were carried out under laboratory conditions including just urban driving cycle. Maximal speed was 50km/h and only pollutant emissions were measured (CO_2 was not tested in EDC) [76]. **Urban Driving Cycle - UDC** also known as an ECE-15 was introduced to reflect driving conditions in European cities (low engine load and exhaust gas temperature). Following Figure 43 shows UDC vehicle speed vs duration curve.

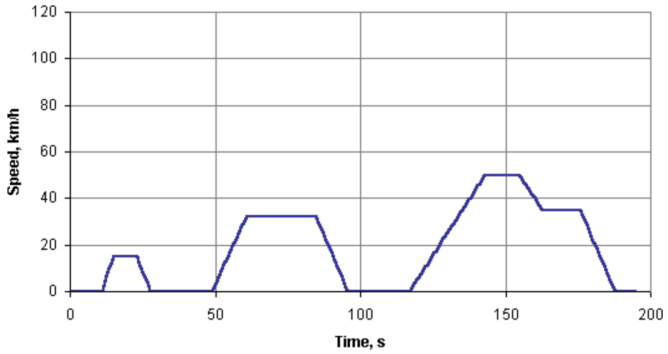
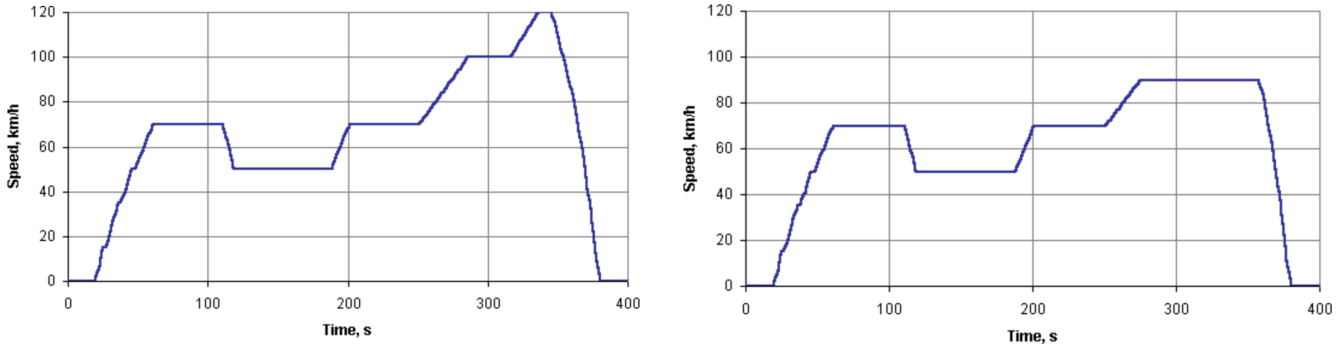


Figure 43: Urban Driving Cycle velocity profile [78].

Afterwards in 1990s, **New European Driving Cycle (NEDC)** came into life with additional **Extra-Urban Driving Cycle - EUDC** (Max. speed 120km/h during 11 seconds [76]). EUDC was intended to reflect high-speed driving modes, with a maximum speed of 120km/h for regular vehicles and 90km/h for low-powered ones. Figure 44 shows EUDC velocity profiles for both regular and low power vehicles.



(a) Regular vehicles.

(b) Low power vehicles.

Figure 44: Extra-Urban Driving Cycle velocity profiles [78].

Characteristics of UDC, EUDC and NEDC are presented in the Table 7.

Characteristics	Unit	UDC	EUDC	NEDC
Distance	km	0,9941	6,9549	**10,9314**
Total time	s	195	400	**1180**
Idle (standing) time	s	57	39	**267**
Average speed (incl. stops)	km/h	18,35	62,59	**33,35**
Average driving speed (excl. stops)	km/h	25,93	69,36	**43,1**
Maximum speed	km/h	50	120	**120**
Average acceleration	m/s2	0,599	0,354	**0,506**
Maximum acceleration	m/s2	1,042	0,833	**1,042**

Table 7: Characteristics of UDC, EUDC and NEDC [78].

The final value of fuel consumption is calculated taking into account both UDC and EUDC. EDC and NEDC tests are performed in laboratory conditions or roller test bench. Currently, New European Driving Cycle is outdated test procedure, it has large tolerance limits and many flexibilities that do not go hand in hand with automotive progress. In NEDC cycle impact of additional features on fuel performance and carbon dioxide emissions are not taken into account. Additionally, nowadays driving manners also have changed comparing to the state when NEDC was designed. All factors discussed above contributed to the development of new driving cycle which represents more precisely everyday driving profiles and is used as global test cycle. From the June 2008, United Nations Economic Commission for Europe (UNECE) and European Union (EU) were developing new test cycle called **Worldwide Harmonized Light Vehicle Test Procedure (WLTP)** which was introduced to type-approval in September 2017 [76]. Figure 45 represents stages of development and implementation of WLTP.

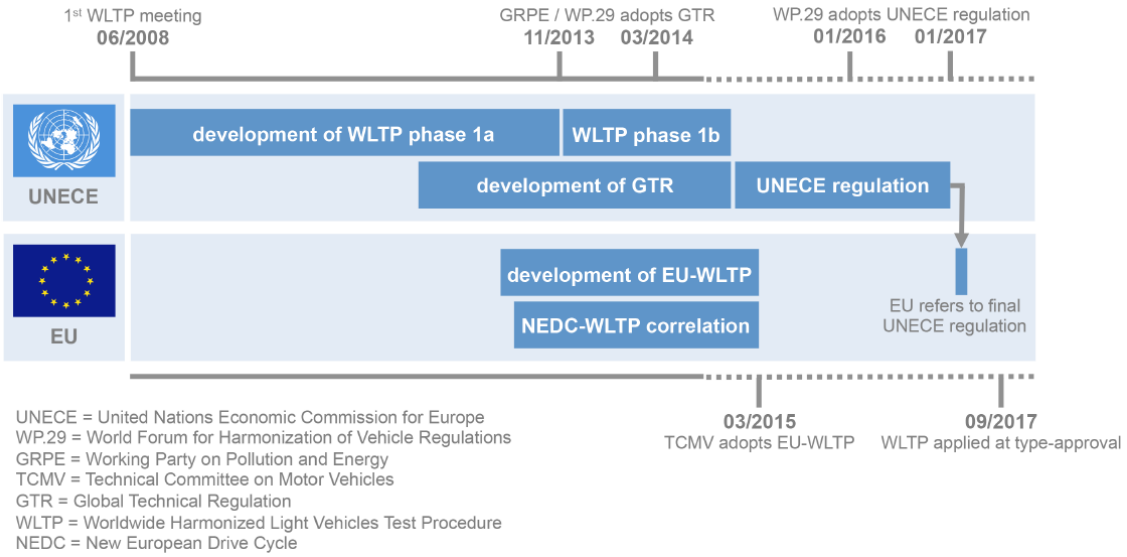


Figure 45: Development and implementation of WLTP into EU regulation [76].

WLTC cycle has four stages: low, medium, high and extra high. Each stage contains different driving phases, stops, acceleration and braking. Additionally, powertrain configurations for each specific car type are tested in WLTP both for most and least economical version [79].

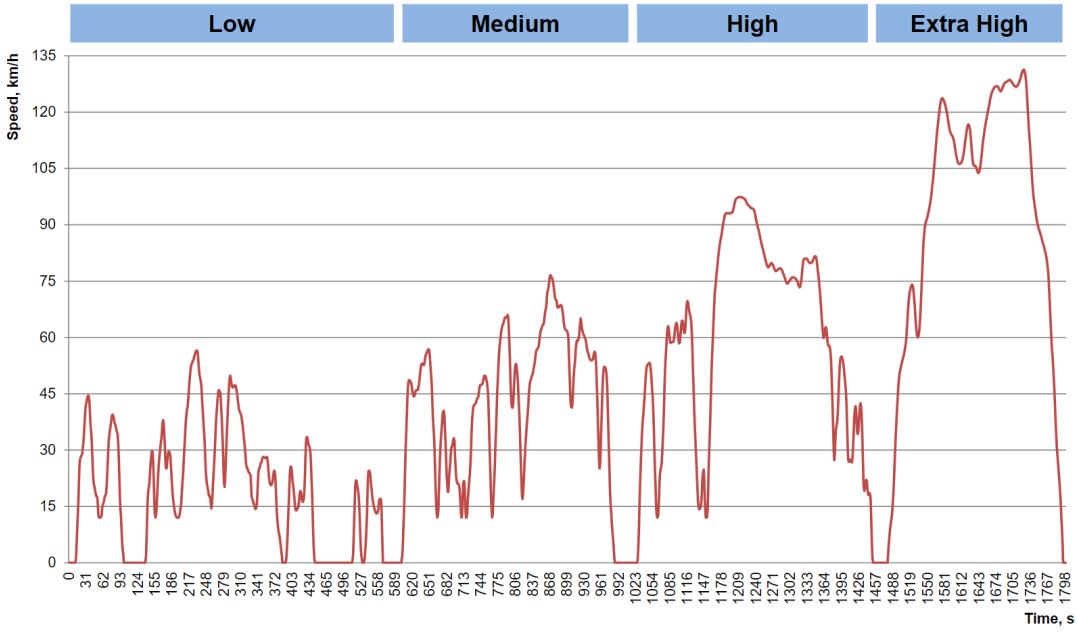


Figure 46: WLTC velocity profile [80].

WLTC and NEDC tests start in cold engine conditions, duration of the cycle is 1180s for NEDC while 1800s for WLTC. WLTC has longer test distances - 23,27km while NEDC 11,03km. Mean velocity is higher in WLTC cycle and reaches 46,5km/h (NEDC has 33,6km/h), while max. velocity is 131,3 km/h. Stop phases are reduced and instead of 12 in NEDC there are only 9 in WLTP [76]. If it comes to comparison of test phases duration, stops and constant driving are reduced in WLTC while acceleration and deceleration is increased. Stops are dropping from 280s in NEDC to 226s in WLTC, where constant driving is reduced from 475s in NEDC to 66s in WLTC. Duration of acceleration has increased from 247s in NEDC to 789s in WLTC, where deceleration from 178s in NEDC to 719s in WLTC [76].

Another very important point is the impact of the WLTP on fuel consumption and CO_2 emissions. NEDC cycle proceeds in the range of low loads and low engine efficiency, additionally shorter distances result in higher cold start effect and manual transmissions at higher engine speeds. As mentioned before decreased stops duration, increased acceleration and higher speeds will result in increased 2.1% CO_2 emissions in WLTP cycle. NEDC does not take into account optional equipment and driver mass, where WLTP assumes 70kg of optional equipment and 55kg of payload [76]. This additionally, will affect CO_2 emissions with 3.7% growth. Last regulatory issued is engine start temperature, NEDC assumes $23°C$, where WLTP $14°C$. Decreasing engine start temperature will produce 1.9% more CO_2 emissions [76]. However, when

the ambient temperature is 23°C, there will be no such an issue. Those factors affect EU 2020 target of 95g/km according NEDC resulting in 102g/km in WLTP at 14°C and 100g/km in 23°C [76]. Time-frame of WLTP implementation is presented in Figure 47. Between 2017 and 2020 there will be a period of double testing (NEDC and WLTP), while after 2020 there will be WLTP testing exclusively.

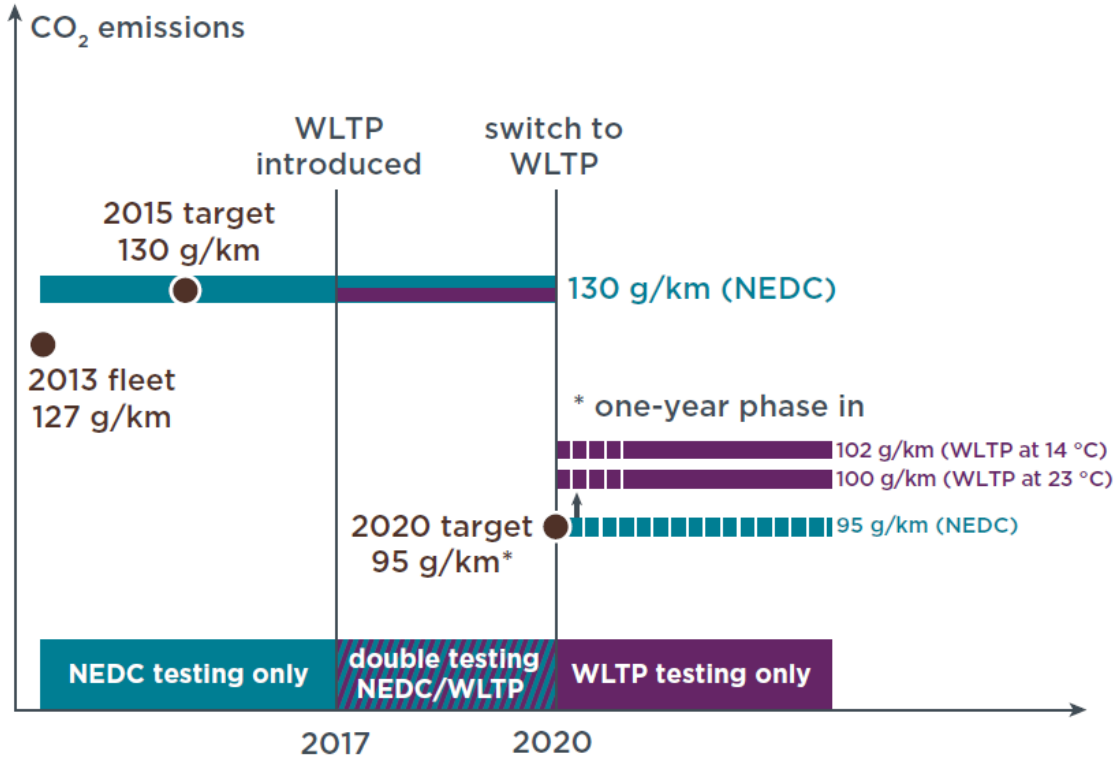


Figure 47: WLTP implementation timeframes [76].

3.6.3 Approach selection

The Project is focused on a **uniform model** that in the reliable and justified way will present impact of fuel properties on fuel consumption and CO_2 emissions. Approach selection is a crucial part of this work, additionally, when the model is required to be designed towards end-use the matter becomes even more important. In the chapter 3.6.1 presented many issues regarding steady state approach. Taking into account all factors, the steady-state approach is not the best option for light and heavy-duty vehicles. Because many parameters play a significant role and affect final state of results. This approach would be more suitable for marine, jet and power plant engines. Modeling based on driving cycles is a better option for the scope of this project. Fuel consumption and related carbon dioxide emissions based on NEDC or WLTP for specified fuel blends are significantly more reliable and represent the real (measured) impact of specified fuel from the end-use point of view. Thus **driving cycles approach is chosen for further considerations and modeling part**.

3.7 Literature study and data selection

Extensive literature study is a solid basement of this project, in order to develop universal and reliable models inseparable part becomes a robust analysis of the most sophisticated available research works. The main purpose of this part was acquiring data for modeling matrix creation. This, in turn, requires data where both properties of different fuel blends were carefully measured and final fuel consumption according to the driving cycles. After analyzing over 100 journal papers for data collection, it was noticed that there is a clear deficiency of publicly available data, which is a very limiting factor for this project. However, 10 sources ([81], [82], [83], [84], [85], [86]), [87], [88], [89], [90]) were selected as the most suitable ones, where finally only 3 were taken into account for data collection (Table 8). First source [87] is an experimental study, where n-butanol blends (max. 20% concentration) with gasoline were tested from the performance and emissions point of view. Second paper [88] in comparison to first one was studying the impact of iso-butanol-gasoline blends (max. 68% concentration), where additionally three ethanol-gasoline blends (E10, E22, and E85) and high octane (RON 102) gasoline fuels were tested. Third source [90] was testing blends of light alcohols with gasoline and their impact on fuel consumption and emissions. Tested fuels were E10 and M15 (15% methanol and 85% gasoline). Information about involved institutions, article, utilized engine types, and properties applied driving cycle procedures and fuels are summarized in the Table 8.

Source	**X** [87]	**Y** [88]	**Z** [90]
Institutions	Indian Oil Corp. Ltd.	Mahle Powertrain, Ltd. BP Powertrain Ltd.	Nanjing University College of Energy and Power Engineering Chinese Research Research Academy of Environmental Sciences
Country **Publisher** **Year**	**India** **SAE** **2016**	**U.K.** **SAE** **2012**	**China** **IEEE** **2016**
	E N G I N E		
Model or year	**475SI**	**14 DOHC 16V**	**2015**
Euro standard	**Euro III**	**Euro IV**	**Euro IV**
Injection method	**MPFI**	**DI**	**MPFI**
Max. Torque [Nm/rpm]	**102/2600**	**280/1700**	**N.S.**
Nr. of cylinders	**4**	**4**	**N.S.**
Nr. Of valves	**16**	**16**	**N.S.**
Bore [mm]	**75**	**82,5**	**N.S.**
Stroke [mm]	**67,5**	**92,8**	**N.S.**
Fuels	**nBu5** **nBu10** **nBu20**	**95RON gasoline** **102RON gasoline** **E10** **E22** **E85** **iBu16** **iBu68**	**E10** **M15**

Table 8: Chosen sources for data collection (N.S. - Not Specified).

3.8 Mathematical modeling

Mathematical modeling of fuel properties impact on engine performance indicators is a core part of this work. In order to select a suitable technique, very important is to understand how different components of the problem affect each other. Based on available sources, it was observed that usually blends, their final properties, and fuel consumption were specified. Thus, blending rate affects final fuels properties and engine performance indicators (purple lines in Figure 48). However, unknown is how particular fuel properties (A, B, C, D Fig. 48) affect engine performance indicators ($\alpha, \beta, \gamma, \delta$ Fig. 48). Subsequently, which properties matter for specified performance indicator and how much do they influence were essential questions.

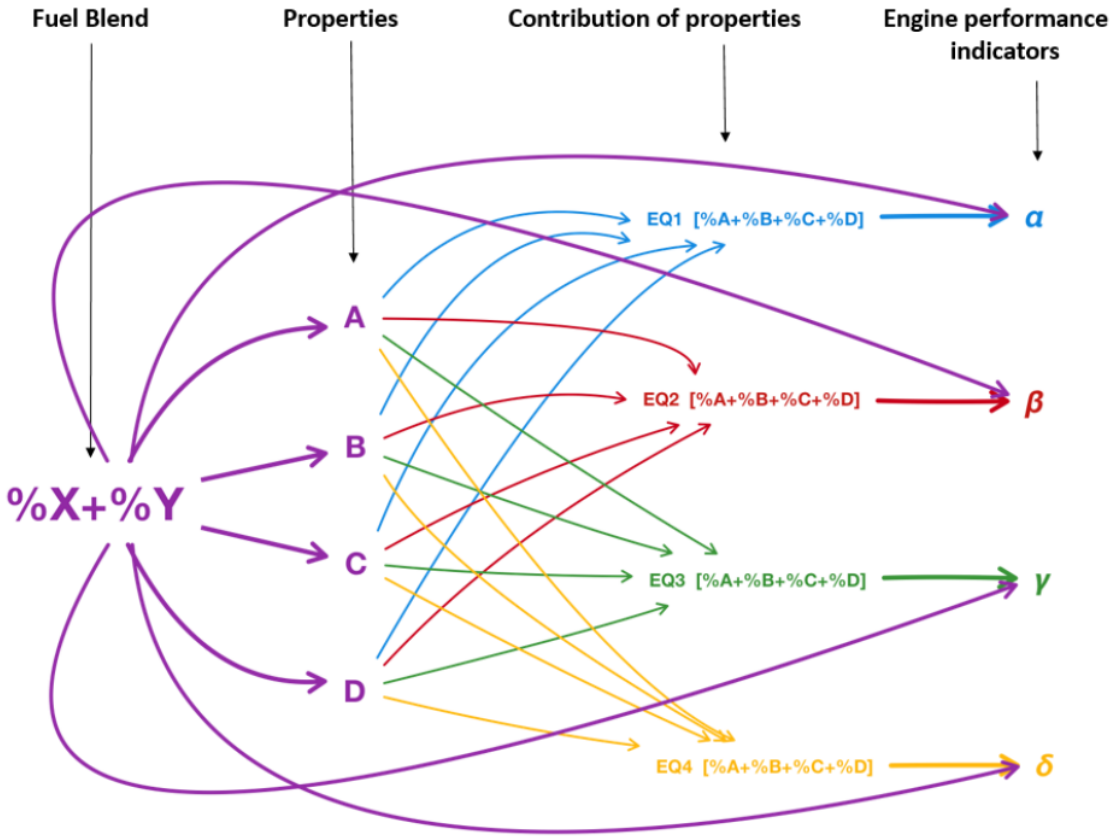


Figure 48: Visualization of the modeling approach.

Regarding earlier discussion this problem manifests itself in the nature of **Multiple Input - Single Output (MISO)** manner. Where input parameters are fuel properties specified in the chapter 3.5.1 and a single output is represented by related fuel consumption (as an engine performance indicator). Very important part is related to the selection of inputs and output representation mode. In order to point the model towards universality, it was decided to represent the fuel blend properties in the form of percentage changes relative to utilized reference gasoline in specified source. The same methodology was applied to output fuel consumption,

thus as a result used gasoline properties were represented by 0% change and their fuel consumption also by 0% change. By implementing this solution into the matrix, created models will represent relative to standard gasoline percentage changes in fuel consumption and carbon dioxide emissions. After careful analysis and consultations with Kai Zenger, it was decided to apply **multi-linear regression** as a modeling method for this problem. Chosen technique is a form of linear regression analysis, that represents the relationship between one dependent variable and several independent variables. Generally, multi-linear regression for n observations is expressed by following equation 3.8.1 [91]:

$$y(x) = \phi_1(x) \cdot \beta_1 + ... + \phi_n(x) \cdot \beta_n + \epsilon(x) \tag{3.8.1}$$

where,
y - dependent variable,
x - independent variable,
$\phi_i(x)$ - explanatory variable,
β_i parameter of explanatory variable,
$\epsilon(x)$ - error.

Eq. 3.8.1 could be converted into matrix form:

$$y = \phi \cdot \beta + \epsilon \tag{3.8.2}$$

With respect to visualized in the Figure 48 approach equation 3.8.1 would take the following form:

$$\alpha = a \cdot A(X) + b \cdot B(X) + c \cdot C(X) + d \cdot D(X) \tag{3.8.3}$$

where,
α - fuel consumption [% change in reference to L/km],
X - alternative fuel volumetric concentration in the blend with standard fossil based fuel,
$A(X)...D(X)$ - fuel property [% change].
$a...d$ - coefficients.

The modeling process is based on the least-square method (equation 3.8), where prediction errors are estimated by scalar function, which is minimized ([91]).

$$J_\theta = \sum_{x=1}^{N} \epsilon^2 = \sum_{x=1}^{N} (y(x) - \phi^T(x) \cdot \theta) \tag{3.8.4}$$

where,
J_θ - least-squares objective function.

Carbon dioxide CO_2 emissions are calculated based on the developed fuel consumption model. The procedure includes multiplication of fuel consumption per 100km with density to obtain the mass of fuel used per 100km. Subsequently, knowing

carbon content and the ratio of carbon dioxide mass to carbon mass, total CO_2 emission per 100km can be calculated. Additionally, the division of output by 100, will represent CO_2 emissions per 1km. The following equation was utilized to perform described calculations:

$$\delta = \alpha \cdot \rho \cdot z \cdot \frac{44}{12} \tag{3.8.5}$$

where,
δ - CO_2 emissions,
ρ - density of the fuel,
z - mass based carbon content in the fuel.

$$z = (x \cdot z_a \cdot \rho_a + (1 - x) \cdot z_d \cdot \rho_d)/\rho_b \tag{3.8.6}$$

where,
x - volumetric fraction (concentration) of alternative fuel;
ρ_a - density of pure alternative fuel;
ρ_d - density of standard diesel;
ρ_b - density of final fuel blend;
z_a - carbon content in alternative fuel;
z_d - carbon content in standard diesel fuel.

3.8.1 Model accuracy and validation procedure

The accuracy of the model is specified by adjusted R-square, standard error, and t-value. Model validation is performed by residual analysis, where values obtained from the model are compared to the theoretical ones and prediction errors are calculated (equation 3.8.7).

$$y(x) = \phi(x) \cdot \theta - \epsilon(x) \tag{3.8.7}$$

where,
x - independent variable;
$y(x)$ - observable output;
$\phi(x)$ - explanatory variable;
θ - parameter (coefficient);
ϵ - error of prediction.

Additionally cross-validation was carried out [92], where part of the available data is used for model development and other part for model validation.

3.8.2 Individual steps of the modeling process

The modeling process is performed in 5 main steps and one optional. The first step includes data selection and preparation, where during second step input and output parameters are converted into percentage changes relative to specified standard fuel. The third step focuses on matrix preparation, which is directly used for mathematical modeling during the fourth step. The validation process is the last one, where a created model is tested. When the model is not good enough, adjusted coefficients are optimized or input data is modified (decreasing/increasing the quantity). The procedure of modeling including all steps is graphically presented in the Figure 49.

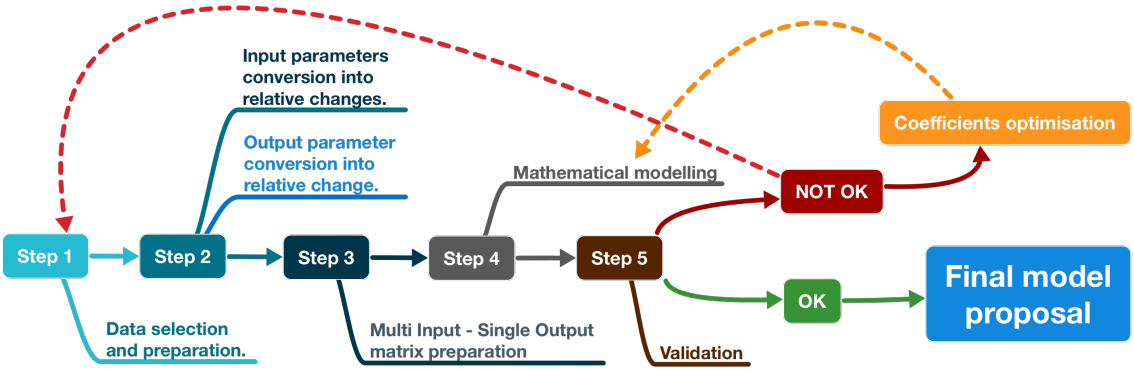


Figure 49: Individual steps of the modeling process.

3.8.3 Tool used for mathematical modeling and data analysis

Data analysis and mathematical modeling are performed in **OriginLAB software**, which is a scientific graphing and data analysis tool [93]. It is worth mentioning that iteration method used for multi-linear regression was **Levenberg-Marquardt Algorithm (LMA)**, which is based on least-squares method. The LMA algorithm is described in detail by Henri P. Gavin from Duke University [94].

4 Results

The results chapter represents outputs of model development and validation stages. Subsequently, the impact of fuel properties on engine performance in extreme cases is presented. The last part includes carbon dioxide emissions prediction and discussion of results. Additionally, fuel consumption and CO_2 emission changes based on developed models are presented for different blends of gasoline with methanol, ethanol, and isobutanol.

4.1 Model development and validation

This section presents results for chosen approach and modeling method. The first point of the analysis aims to indicate how octane number, a heat of vaporization, lower heating value (volume based) and auto-ignition temperature affect fuel consumption individually. The output for chosen 3 sources ([87], [88] and [90]) is presented in the Figure 50.

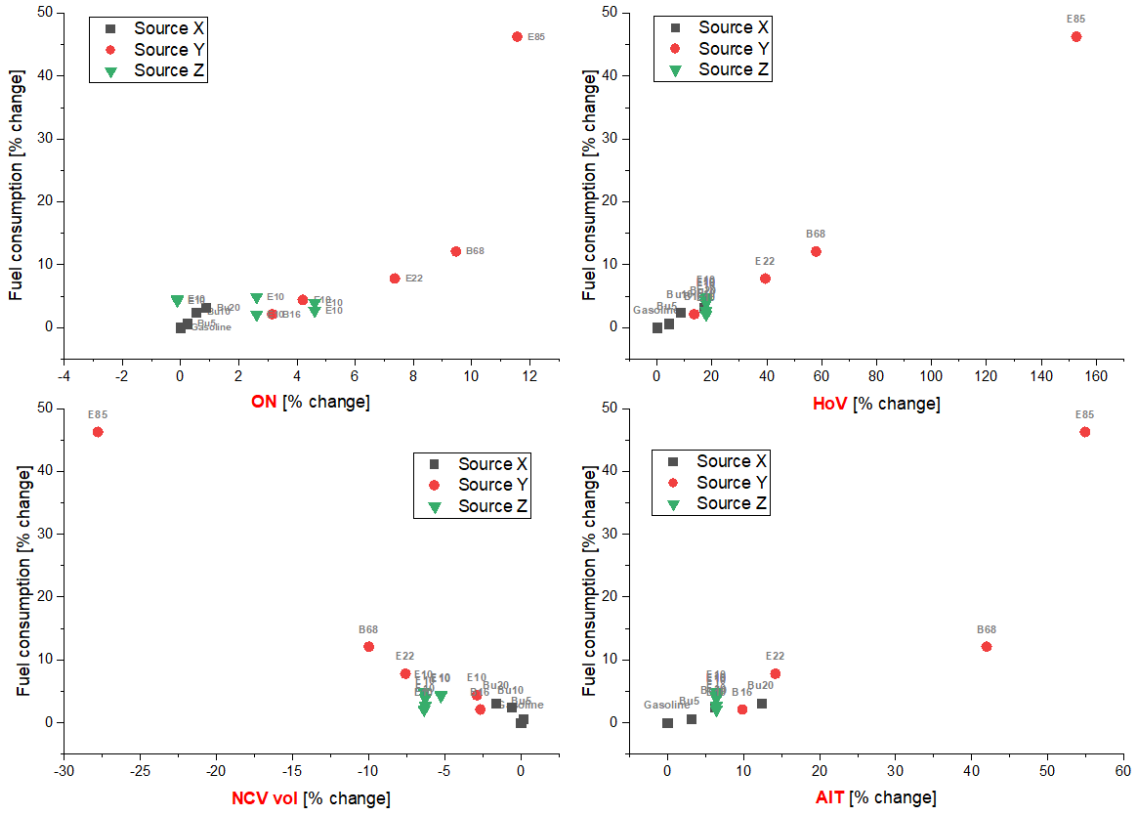


Figure 50: Fuel consumption percentage change dependent on ON, HoV, NCV vol and AIT changes for chosen sources: X-[87], Y-[88] and Z-[90].

The growth of auto-ignition temperature and heat of vaporization increases fuel consumption linearly. The increase of net calorific value results in a significant drop in fuel consumption, where the relation is also linear. Octane number affect

is from the first sight surprising, because with the growth of ON, fuel consumption increases. However, this is caused by NCV shielding, high octane number blends (like E85) have low net calorific value, which is straightforward related to the higher fuel consumption. Figure 51 represents final data that were used to create the models, fuel consumption based on sources and predicted by the model. Additionally, the last column represents prediction errors and average error based on all cases.

SOURCE	DRIVING CYCLE	FUELS	FUEL PROPERTIES				FUEL CONSUMPTION		
			ON	HoV	NCVvol	AIT	BASED ON SOURCES	MODEL PREDICTION	ERROR [%]
			% CHANGE					% CHANGE	
X	NEDC	Gasoline	0,00	0,00	0,00	0,00	0,00	0,00	0,000
		nBu5	0,22	4,27	0,16	3,09	0,60	1,17	0,566
		nBu10	0,55	8,53	-0,62	6,17	2,44	2,16	0,284
		nBu20	0,88	17,07	-1,60	12,34	3,12	4,34	1,222
Y	NEDC	E10	4,21	17,97	-2,87	6,46	4,36	4,34	0,016
		E22	7,37	39,53	-7,56	14,21	7,76	10,08	2,315
		E85	11,58	152,72	-27,78	54,90	46,26	45,52	0,737
		iBu16	3,16	13,65	-2,64	9,87	2,09	2,34	0,257
		iBu68	9,47	58,02	-9,97	41,96	12,08	11,63	0,445
Z	WLTC cold	E10	-3,01	17,97	-3,48	6,46	5,73	6,97	1,248
		M15	7,07	43,00	-4,15	12,08	12,41	12,55	0,141
	WLTC hot	E10	-3,01	17,97	-3,48	6,46	6,57	6,97	0,401
		M15	7,07	43,00	-4,15	12,08	12,85	12,55	0,300
								Average error [%]:	0,610

Figure 51: MISO matrix (values expressed in percentage changes) for mathematical modeling process and model outputs.

The equation 4.1.1, represents obtained function:

$$\alpha = -0,377 \cdot A + 0,419 \cdot B + 0,151 \cdot C - 0,182 \cdot D \tag{4.1.1}$$

Where;
α - relative change of fuel consumption [% change in reference to L/km].
A - relative change of octane number [%].
B - relative change of heat of vaporisation [%].
C - relative of net calorific value (volume based) [%].
D - relative change of autoignition temperature [%].

Coefficient of determination (R-square) is equal 0,994, where **adjusted R-square: 0,992**. Both values are very high and represent good accuracy of the model, especially when taking into account limited number of input data. Adjusted coefficients and their standard errors are listed in the Table 9.

Coefficient	Value	Standard Error	t-Value	Prob>|t|
A	-0,377	0,118	-3,196	0,011
B	0,419	0,044	9,532	0,000
C	0,151	0,227	0,663	0,524
D	-0,182	0,050	-3,628	0,006

Table 9: Values of adjusted coefficients and their uncertainty.

The Table 10 represents modeling accuracy and validation procedure. The First column contains the results of modeling for sources X, Y and Z. Three subsequent columns were used for cross-validation purposes, where from each column one different article was deducted. Validation procedure proved that coefficients are strongly dependent on input data. In the case of NCVvol, it could be noticed that when excluding source Z, the model adjusts -0,568 for NCVvol. Which is not only different number but it also has a negative sign. If it comes to other properties, their sign is not changing during validation procedure. In all cases R-square values are very high (above 0.99), this contributed also to low average errors.

	SOURCES			
	XYZ	YZ	XZ	XY
NCV vol	0,151	0,338	-0,112	-0,568
ON	-0,377	-0,451	-0,171	-0,742
HoV	0,419	0,446	0,382	0,282
AIT	-0,182	-0,146	-0,250	-0,076
R-square	**0,994**	**0,995**	**0,993**	**0,997**
Adj. R-square	**0,992**	**0,992**	**0,988**	**0,996**
Average error [%]	**0,610**	**0,640**	**0,644**	**1,427**

Table 10: The models and validation procedure.

The case XYZ includes all sources and the adjusted coefficient for NCVvol is 0,151. This unexpected value is a result of the interrelation between chosen properties and character of modeling. Which adjusts the coefficients so as to obtain the highest accuracy (R-square) not taking into account their real impact on fuel consumption (FC). From the theoretical point of view, FC is strongly dependent on the energy content of the fuel. Amount of fuel introduced into the engine (mass flow) is thus straightforward related to NCV. In order to direct the model towards more realistic impacts, the interrelation between NCVvol and fuel consumption was examined (Figure 52).

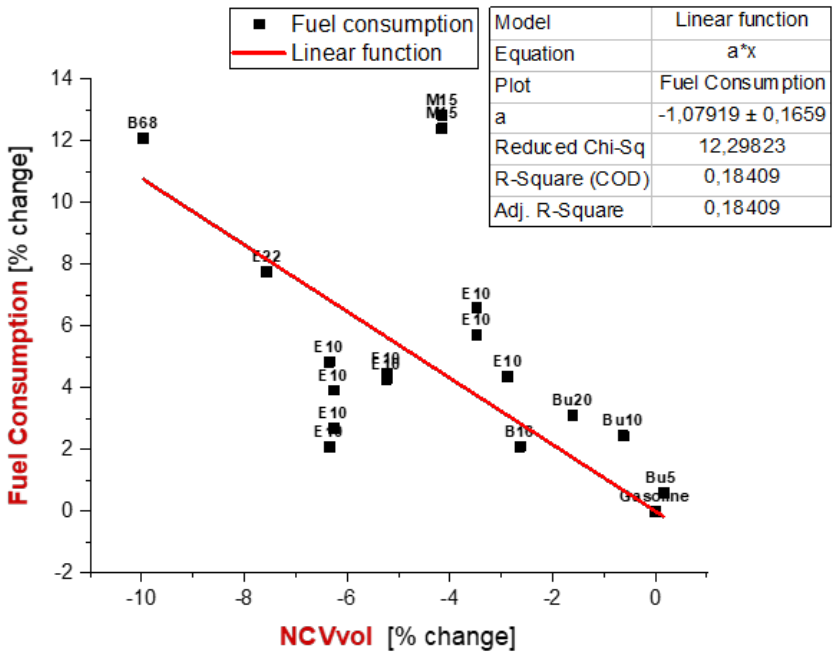


Figure 52: Impact of NCVvol on fuel consumption, based on sources A, B, C and D.

The relationship turned out to be linear (proportional), and thus multi-linear regression was performed again with a fixed coefficient of -1 by net calorific value (volume based). The **Final model's** accuracy is slightly lower compared to the previous case. Nevertheless it is still very high: **R-square value is equal 0,97816** and **adjusted R-Square value is 0,97379** (Figure 11).

Coefficient	Value	Standard Error	t-Value	Prob>|t|
a	-0,09554	0,19339	-0,49404	0,63195
b	0,22068	0,03691	5,97857	1,36E-04
c	-1	0	–	–
d	-0,24562	0,09031	-2,71981	0,02157

Table 11: Final model's adjusted coefficients values and their uncertainty.

Final model could be expressed in the following form:

$$\alpha = -0,09554 \cdot A + 0,22068 \cdot B - 1 \cdot C - 0,24562 \cdot D \tag{4.1.2}$$

Where;
α - relative change of fuel consumption [% change in reference to L/km].
A - relative change of octane number [%].
B - relative change of heat of vaporisation [%].
C - relative of net calorific value (volume based) [%].
D - relative change of autoignition temperature [%].

The final model predicts significantly more precise fuel consumption compared to the first one. Additionally, the average error has strongly decreased, from 2,2% in the first model to 1,222% in the final one. Validation table is presented in the Figure 53.

SOURCE	DRIVING CYCLE	FUELS	FUEL PROPERTIES				FUEL CONSUMPTION		
			ON	HoV	NCVvol	AIT	BASED ON SOURCES	MODEL PREDICTION	ERROR [%]
			% CHANGE				% CHANGE		
X	NEDC	Gasoline	0,00	0,00	0,00	0,00	0,00	0,00	0,000
		nBu5	0,22	4,27	0,16	3,09	0,60	0,00	0,604
		nBu10	0,55	8,53	-0,62	6,17	2,44	0,94	1,503
		nBu20	0,88	17,07	-1,60	12,34	3,12	2,25	0,863
Y	NEDC	E10	4,21	17,97	-2,87	6,46	4,36	4,85	0,489
		E22	7,37	39,53	-7,56	14,21	7,76	12,09	4,327
		E85	11,58	152,72	-27,78	54,90	46,26	46,89	0,627
		iBu16	3,16	13,65	-2,64	9,87	2,09	2,92	0,836
		iBu68	9,47	58,02	-9,97	41,96	12,08	11,56	0,520
Z	WLTC cold	E10	-3,01	17,97	-3,48	6,46	5,73	6,14	0,418
		M15	7,07	43,00	-4,15	12,08	12,41	10,00	2,413
	WLTC hot	E10	-3,01	17,97	-3,48	6,46	6,57	6,14	0,429
		M15	7,07	43,00	-4,15	12,08	12,85	10,00	2,854
								Average error [%]:	1,222

Figure 53: Final model validation table.

The cross-validation procedure results are presented in the Table 12. The First column includes all sources (X, Y, and Z), the second one excludes source X, third includes X and Z, whereas the last one only X and Y. It could be observed that input data have a very strong influence on final model's coefficients and accuracy. The highest R-square belongs to the XY case, whereas the lowest average error is observed in YZ case.

	SOURCES			
	XYZ	YZ	XZ	XY
NCV vol	-1,000	-1,000	-1,000	-1,000
ON	-0,096	-0,068	0,111	-0,801
HoV	0,221	0,227	0,222	0,197
AIT	-0,246	-0,272	-0,154	-0,043
R-square	**0,978**	**0,976**	**0,992**	**0,997**
Adj. R-square	**0,974**	**0,968**	**0,989**	**0,996**
Average error [%]	1,222	1,254	2,163	1,786

Table 12: The cross-validation of final model.

4.2 Impact of fuel properties on fuel consumption in extreme cases

Calculation of each property maximal contribution to fuel consumption could help to understand how much they affect. Hence, maximal change of each fuel property multiplied by a coefficient obtained from modeling represents the maximal possible impact on fuel consumption. The analysis shows that HoV is the highest contributor (0,34), NCV vol is the second one (-0,28), subsequently AIT (-0,13) and least influence is by ON (-0,01). Additionally, the total share of FC impact among properties was calculated (Table 13).

Property	Coefficient	Max. change	Max. Impact on Fcvol	Absolute Value	Total share
ON	-0,096	11,58 %	-1,11 %	0,01	1,5 %
HoV	0,221	152,72 %	33,70 %	0,34	44,3 %
NCV vol	-1,000	-27,78 %	27,78 %	0,28	36,5 %
AIT	-0,246	54,90 %	-13,48 %	0,13	17,7 %

Table 13: Maximal possible impact of properties on fuel consumption.

4.3 Carbon dioxide emissions

Carbon dioxide emissions calculation is based on the fuel consumption model, density, carbon content and mass ratio of CO_2 and C. Table 14 represents carbon dioxide emissions for chosen fuels and fuel blends. Very interesting results can be observed for methanol fuels, M85 and E100, where despite significantly increased fuel consumption, carbon dioxide emissions are lower compared to pure gasoline. This is mainly caused by a high ratio of hydrogen/carbon in methanol and ethanol fuels, where methanol has the highest and thus the lowest emissions of CO_2.

Fuel	Density	C [%m/m]	FC [% change]	CO2 [% change]
M10	754,60	79,63 %	9,40 %	3,63 %
M20	759,20	74,95 %	18,81 %	6,26 %
M40	768,40	65,59 %	37,61 %	8,55 %
M85	789,10	44,52 %	79,93 %	-0,81 %
M100	796,00	37,50 %	94,03 %	-8,40 %
E5	752,20	82,70 %	2,60 %	0,83 %
E10	754,40	81,90 %	5,21 %	1,57 %
E20	758,80	77,87 %	10,42 %	2,78 %
E60	776,40	64,98 %	31,25 %	4,02 %
E85	787,40	56,93 %	44,27 %	1,87 %
E100	794,00	52,10 %	52,08 %	-0,51 %
iBu5	752,60	83,33 %	1,22 %	0,32 %
iBu10	755,20	82,36 %	2,44 %	0,61 %
iBu50	776,00	74,56 %	12,19 %	2,20 %
iBu85	794,20	67,73 %	20,73 %	2,45 %
iBu100	802,00	64,80 %	24,39 %	2,23 %

Table 14: Fuel consumption and carbon dioxide emissions for different fuels and fuel blends based on the final model.

5 Conclusions

This thesis corresponds to the problem of how particular fuel properties affect engine performance and carbon dioxide emissions. The main contribution of this work relates to the impact of fuel and fuel blends properties on SI engine performance and carbon dioxide emissions. In order to approach to this problem it was important to pass through the extensive studies of engine characteristics, combustion process and related issues, fuel characteristics, exhaust emissions and their control techniques. That part strengthened the theoretical basis and enabled deeper understanding of the problem from the technical point of view. Subsequently, it was finalized within the background of this work. Second stage included data collection, where recent articles, available journal papers and different databases were selected and subsequently analyzed. Additionally, meetings with fuel producers such as NESTE, ST1 and OEMs: AVL and VOLVO were very valuable. During meetings general ideology was confirmed by industry and enriched with precious advice. Structure of the problem contains three main parts; fuel properties, engine and exhaust emissions. If it comes to fuels, very important was to chose renewable and commercially available fuels with economic potential. Additionally, they should be drop-in fuels at least within the range of specified blending wall. After deep analysis, it turned out that the most prominent alternative fuels for SI engines are alcohols, with distinction of methanol, ethanol and butanol. Nevertheless, they have own challenges that should be considered in further analysis. Methanol is a promising alternative fuel which has the highest hydrogen/carbon ratio among other alcohols. This results in the lowest carbon dioxide emissions - section 4.3. However, toxicity is a significant disadvantage. Ethanol-gasoline blends are the most common and available ones, where EN228 standard allows maximum 10% concentration [17]. Additionally, it is important to take into account necessary engine modifications for larger concentrations (section 3.3.2). Propanol in comparison to ethanol is more expensive from the production point of view, thus it was not considered as a potential fuel. Subsequent fuel is butanol, which has many advantages over other alcohols. Butanol properties are the closest to gasoline, which allows to utilize it in SI engines without major modifications, even in the range of higher concentrations. Another part related to fuels was selection of the most relevant properties. After analysis in section 3.5.1 and initial modeling, it was observed that the most relevant are octane number, the heat of vaporization, net calorific value (volume based) and autoignition temperature. These properties affect the most apparently fuel consumption and carbon dioxide emissions, what was closer examined in the subsequent part. From the very beginning of the engine performance analysis, it was realized that there is a lack of information in the literature about part of used fuels properties. In order to complete the missing data fuel blend property calculator was created (section 3.5.2). Based on mathematical models, properties of two-component blends (reference gasoline and alcohols) could be calculated with very high accuracy. Essential part of this work, was selection of approach for engine performance modeling. In general there were three possibilities, steady state, driving cycles and combustion characteristics based approaches. Steady-state approach is connected with many limitations such as strong sensitivity of brake

specific fuel consumption and brake thermal efficiency on mean piston speed and brake mean effective pressure. Additionally, as presented in the Figure 41, different sources represent different behavior of BSFC and BTE with growing ethanol concentration. If it comes to combustion characteristics, thousands of parameters (physics of processes and chemistry of proceeding reactions) influence final state of results, which makes this approach extremely difficult. It was decided to continue work with driving cycles approach, which turned out to be the best solution. Driving cycles approach makes final models significantly more uniform and represents fuel properties impact on real driving fuel consumption from the end-use point of view. That is exactly the main purpose of this work and objective O5 (WP5) of ADVANCE*FUEL* project. Additionally, new test procedure called WLTP, contributes to even higher reliability, by proceeding more up-to-date measurements comparing with NEDC cycle. However, availability of appropriate data from literature proved to be a strong limitation of the project. After extensive studies, only three literature sources ([87], [88], [90]) were used for final model development. The subsequent stage was focused on system identification and mathematical modeling method selection. It was observed that the problem has multiple inputs (fuel properties) and single output (fuel consumption) character. Thus it was decided to apply multi-linear regression for modeling purposes. Subsequently, carbon dioxide emissions, are calculated based on fuel consumption and carbon content of the blend. In the chapter: exhaust gas composition 2.4.1 it was presented that roughly all carbon is converted to carbon dioxide, where the remaining part, which is less than 1%, is emitted in the form of pollutants such as hydrocarbons (0.2%) or carbon monoxide (0.7%). This evidence assures the correctness of methodology and reliability of CO_2 emissions prediction. In order to make the model uniform, it was decided to treat both fuel blend properties and fuel consumption as a percentage change, relative to the standard fuel (gasoline) used in the specified source. This practice helped also to reduce the impact of test engine characteristics. Furthermore, the accuracy of the model was defined by the coefficient of determination (R-square), standard error and t-value. Subsequently, validation process was performed by residual and cross-validation analysis. Model development is a core part of this work, where based on all reflections, the model was created. The modeling process was distributed into two steps, first one was aiming at the pure adjustment of linear function during multi-linear modeling. Where the second parts' purpose was to evaluate how real are adjusted coefficients. Despite the fact that first step represented higher accuracy (R-square) and lower average error, it was observed that for chosen sources, the coefficient of NCVvol is positive (0,151). The fundamental goal of the engine is a conversion of one form of energy into another. The growth of energy content of the fuel (NCVvol) should thus result in lower fuel consumption (negative sign of the coefficient). The relation between fuel consumption and NCVvol was examined separately, and the result confirmed considerations (coefficient of -1). Taking this into account, multi-linear regression was repeated with the fixed coefficient of -1 by NCVvol. The final modeling adjusted coefficients of 0,096 for ON, 0,221 for HoV and -0,246 for AIT. The accuracy of the proposed model is slightly lower (but still very high, R-square $>$ 0,97) compared to the case where NCVvol is not controlled. However, the model is significantly

more realistic and precise, especially when considering very similar blends with small differences in calorific content. The validation procedure proved that coefficients are strongly dependent on input data. The impact can not only change the values of different coefficients but also their sign (ON coefficient in XZ case). The subsequent step after model development and validation was to examine the impact of fuel properties on fuel consumption in extreme cases. It was observed that the most influential is the heat of vaporization (when talking about extreme changes), with the maximum possible impact of 33,70%. The second largest contributor is a net calorific value 27,78% affect of FC. The third in turn is autoignition temperature, max 13,48%, where the least influential is ON 1,11%. All properties together are responsible for the total impact on engine performance (fuel consumption). However, it is important to remember that fuel properties are also interrelated and change of one property would influence on others. The last point of the results part include CO_2 emission predictions for different blends of gasoline with alcohols (methanol, ethanol, isobutanol). Very interesting results were observed for high concentration methanol-gasoline blends, where despite significantly increased fuel consumption, carbon dioxide emissions are lower compared to pure gasoline. This is the consequence of very high (the highest among alcohols) hydrogen-carbon ratio of methanol. Final results are acceptable, especially when taking into account that measurements are coming from different parts of the world, tests were performed in different engines and utilized fuel blends were different. It is also worth noting that even standard gasoline that was used in each source differs significantly.

5.1 Limitations

Main restrictions of this work include a limited number of available studies, where according to NEDC or WLTP different alternative fuels are tested. The final model is very sensitive to input data, despite the high accuracy of the model, it could be further upgraded with a larger amount of input data. Additionally, more input data would enable the possibility of deeper cross-validation analysis. Important is also to pay attention to the fact that WLTP is a new procedure that came into life on September 2017, thus there are significantly fewer data of WLTP studies than NEDC, which is currently over 28 years on the market. Another constraint could be assigned to fuel blend properties calculator errors and the fact that some fuel properties assumed by FBPC could differ in reality from the ones utilized in a specific article. The main reasons behind that kind of effects rely on differences between used in the given source gasoline and properties of base gasoline taken into FBPC models. The last perceived limitation could be related to the linear approach, extended studies dedicated to relations between each fuel property and engine performance may lead towards some non-linear relations. Development of new models based on non-linear modeling could potentially improve even further final body of the function and its accuracy.

5.2 Importance of this research

This research brings new knowledge about how particular fuel and fuel blend properties affect engine performance (fuel consumption) and carbon dioxide emissions. Developed models provide new possibilities for predicting the impact of fuels (characterized by different properties than standard well-tested fuels) on end-use. Which is of particular importance when talking about new advanced transport fuels for existing SI engines. Developed model, gives additionally possibility of manipulation with properties in order to achieve the most optimal fuel consumption or the lowest environmental impact. They can bring significant benefits for fuel producers and decision makers by giving first sight impact of considered or designed solutions. As a further consequence, the model can help to bypass the commercialization barriers of many renewable transport fuels. The fuel blend properties calculator, on the other hand, can support the prediction of fuel blend properties characterized by very high accuracy. This research work, have a great potential for supporting actions towards cleaner road transportation and local environment in many polluted cities around the world.

5.3 Future recommendations

In further expansion stages even stronger cooperation with industry especially fuel producers and OEMs would be of high priority. Essential data required for further development are in majority not available for public, thus arranging closer cooperation may lead towards game-changing results. It would be beneficial to make a WLTC tests of ethanol and butanol fuel blends with gasoline. Afterward, create models from domestic research and compare the results. This could be also a good base for validation purposes and extension of the matrix. Another important area of research could be testing of other properties impact on fuel consumption and extensive analysis of what modifications would be required to adjust the engine for high concentration methanol, ethanol or butanol blends. Subsequently, it would be highly recommended to carry on experimental research where different properties impact could be approved empirically. From the technical point of view, this could be achieved by preparation of fuel blends samples with differences in specified property or group of interrelated properties, while keeping constant other properties that are not interrelated. Afterward, running WLTC tests for each sample. That kind of studies could support understand fo exact relations between interrelated properties.

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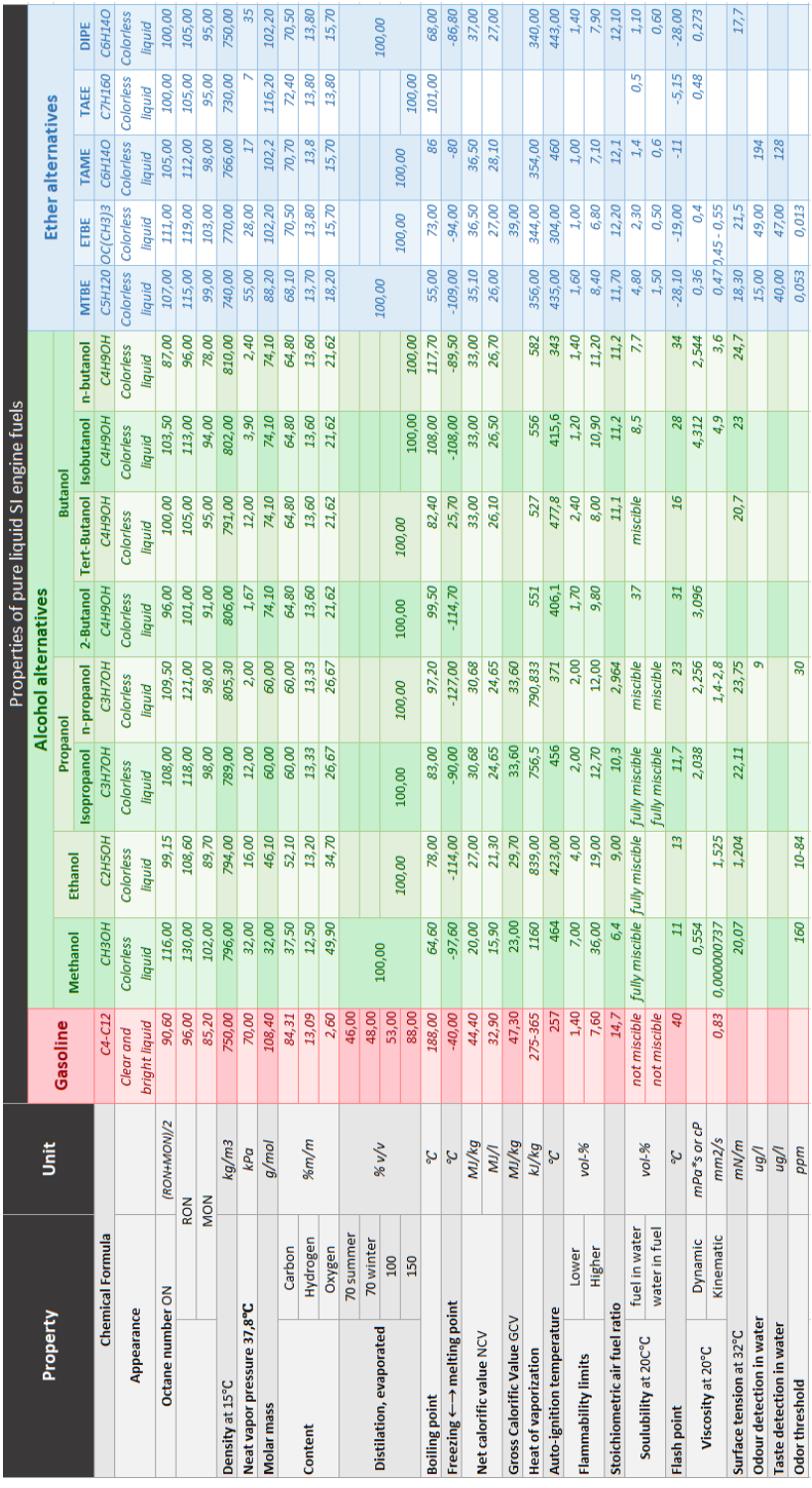
A Appendix



Property	Unit	Gasoline	Alcohol alternatives										Ether alternatives				
			Methanol	Ethanol	Propanol		Butanol						MTBE	ETBE	TAME	TAEE	DIPE
					Isopropanol	n-propanol	2-Butanol	Tert-Butanol	Isobutanol	n-butanol							
Chemical Formula		C4-C12	CH3OH	C2H5OH	C3H7OH	C3H7OH	C4H9OH	C4H9OH	C4H9OH	C4H9OH			C5H12O	OC(CH3)3	C6H14O	C7H16O	C6H14O
Appearance		Clear and bright liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid			Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid	Colorless liquid
Octane number ON	(RON+MON)/2	90,60	116,00	99,15	108,00	109,50	96,00	100,00	103,50	87,00			107,00	111,00	105,00	100,00	100,00
RON		96,00	130,00	108,60	118,00	121,00	101,00	105,00	113,00	96,00			115,00	119,00	112,00	105,00	105,00
MON		85,20	102,00	89,70	98,00	98,00	91,00	95,00	94,00	78,00			99,00	103,00	98,00	95,00	95,00
Density at 15°C	kg/m3	750,00	796,00	794,00	789,00	805,30	806,00	791,00	802,00	810,00			740,00	770,00	766,00	730,00	750,00
Neat vapor pressure 37,8°C	kPa	70,00	32,00	16,00	12,00	2,00	1,67	12,00	3,90	2,40			55,00	28,00	17	7	35
Molar mass	g/mol	108,40	32,00	46,10	60,00	60,00	74,10	74,10	74,10	74,10			88,20	102,20	102,2	116,20	102,20
Content Carbon	%m/m	84,31	37,50	52,10	60,00	60,00	64,80	64,80	64,80	64,80			68,10	70,50	70,70	72,40	70,50
Content Hydrogen	%m/m	13,09	12,50	13,20	13,33	13,33	13,60	13,60	13,60	13,60			13,70	13,80	13,8	13,80	13,80
Content Oxygen	%m/m	2,60	49,90	34,70	26,67	26,67	21,62	21,62	21,62	21,62			18,20	15,70	15,70	13,80	15,70
Distillation, evaporated 70 summer	% v/v	46,00															
Distillation, evaporated 70 winter	% v/v	48,00	100,00										100,00				100,00
Distillation, evaporated 100	% v/v	53,00		100,00	100,00	100,00	100,00	100,00	100,00	100,00				100,00	100,00	100,00	
Distillation, evaporated 150	% v/v	88,00															
Boiling point	°C	188,00	64,60	78,00	83,00	97,20	99,50	82,40	108,00	117,70			55,00	73,00	86	101,00	68,00
Freezing ←→ melting point	°C	-40,00	-97,60	-114,00	-90,00	-127,00	-114,70	25,70	-108,00	-89,50			-109,00	-94,00	-80		-86,80
Net calorific value NCV	MJ/kg	44,40	20,00	27,00	30,68	30,68		33,00	33,00	33,00			35,10	36,50	36,50		37,00
	MJ/l	32,90	15,90	21,30	24,65	24,65		26,10	26,50	26,70			26,00	27,00	28,10		27,00
Gross Calorific Value GCV	MJ/kg	47,30	23,00	29,70	33,60	33,60								39,00			
Heat of vaporization	kJ/kg	275-365	1160	839,00	756,5	790,833	551	527	556	582			356,00	344,00	354,00		340,00
Auto-ignition temperature	°C	257	464	423,00	456	371	406,1	477,8	415,6	343			435,00	304,00	460		443,00
Flammability limits Lower	vol-%	1,40	7,00	4,00	2,00	2,00	1,70	2,40	1,20	1,40			1,60	1,00	1,00		1,40
Flammability limits Higher	vol-%	7,60	36,00	19,00	12,70	12,00	9,80	8,00	10,90	11,20			8,40	6,80	7,10		7,90
Stoichiometric air fuel ratio		14,7	6,4	9,00	10,3	2,964		11,1	11,2	11,2			11,70	12,20	12,1		12,10
Soulubility at 20°C fuel in water	vol-%	not miscible	fully miscible	fully miscible	fully miscible	miscible	37	miscible	8,5	7,7			4,80	2,30	1,4	0,5	1,10
Soulubility at 20°C water in fuel	vol-%	not miscible			fully miscible	miscible							1,50	0,50	0,6		0,60
Flash point	°C	40	11	13	11,7	23	31	16	28	34			-28,10	-19,00	-11	-5,15	-28,00
Viscosity at 20°C Dynamic	mPa*s or cP		0,554		2,038	2,256	3,096		4,312	2,544			0,36	0,4		0,48	0,273
Viscosity at 20°C Kinematic	mm2/s	0,83	0,000000737	1,525		1,4-2,8			4,9	3,6			0,47	0,45 - 0,55			
Surface tension at 32°C	mN/m		20,07	1,204	22,11	23,75		20,7	23	24,7			18,30	21,5			17,7
Odour detection in water	ug/l					9							15,00	49,00	194		
Taste detection in water	ug/l												40,00	47,00	128		
Odor threshold	ppm		160	10-84		30							0,053	0,013			

Figure A1: Properties of pure liquid SI engine fuels. Made based on following sources: [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [44], [45], [46], [47], [48], [49], [50], [51], [52], [53], [54], [55], [56], [57].